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THE PHYSICAL STRUCTURE OF ALLOYS

THE PHYSICAL STRUCTURE OF ALLOYS

*An Introduction to Modern Physico-
Chemical Theories*

By

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PREFACE

THE scientific study of the structure of alloys was first developed by the physical chemist and the metallurgist. It is now tending to become the province of the physicist and mathematician. The student who is interested in this important subject is often inclined to feel that, until he has specialised in all these branches of science, he cannot hope to understand its recent developments. The author thinks, however, that this small book will help to indicate to the not, of necessity, specialist reader—to the man engaged in industry and to the student at the laboratory bench—the main directions along which progress has been, and indeed is being, made. He feels that his work in writing the book will be well repaid if he has succeeded in presenting his subject matter in such a way that it will be of direct use to practising and student metallurgists, and to similar groups of chemists and physicists, who are now becoming increasingly concerned with metals and alloys. He would here point out that it is only in the manner and order of the presentation of his subject that he would lay any claim to originality of treatment. The author hopes that this little book will help, if only in a small way, to convey to students of Metallurgy, Chemistry and Physics a broad outline of the contributions made within recent years by their predecessors towards the solving of what were some of the bewildering problems of the science of alloys.

In addition to the students of all ages already referred to, the book should be of some value to those whose immediate concern is the attainment of a professional qualification. It would, from this viewpoint, help to supplement the standard text-books of university and technical college students who are either working for degrees in Metallurgy, Chemistry or Physics, or for examinations of the standard of that of the

Associateship of the Royal Institute of Chemistry. It may also help to extend the range of study of the candidate for the City and Guilds Examination in "Principles of Physical Metallurgy."

Although a large number of books, some of which are suggested for further reading, have been consulted during the preparation of this one, the author feels that he probably owes more to the writings of Dr. Hume-Rothery than to those of any other single individual. This little book will help to bridge the gap between the student's text-book and the specialist publications of Dr. Hume-Rothery and other workers in this field.

The author would like to thank Dr. R. S. Morrell for reading his original MS. and for making several useful suggestions for its improvement. He would, however, point out that any opinions expressed in the book are his own; responsibility for them he alone must accept. He would thank Mr. E. A. Shipley and Mr. J. Poole for help with the line diagrams. The former, one of his old students at Coventry, was able to supply most of them, and his keenness to produce neat diagrams was only equalled by his zeal for understanding the theory behind them. The author, in conclusion, thanks those who have helped with the illustrating plates—Messrs. Metropolitan-Vickers Electrical Co., Ltd., for Figs. 8, 9, 13 and 26 and the Royal Institution for Figs. 34 and 35. Finally, he would dedicate this book to his father, whose help and encouragement he has always been most freely given.

C. E. BEYNON

WOLVERHAMPTON,
1945

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CHAPTER I

THE STRUCTURE OF THE ATOM

The Electron. The intimate relationship between chemistry and electricity was first demonstrated by Michael Faraday in 1834 when he showed that the liberation by electrolysis of the gram equivalent weight of any element requires the passage of 96,500 coulombs (amp. secs.), a quantity of electricity known as *the faraday*. It was pointed out some fifty years later by Johnstone Stoney that the charge on the individual ions could be calculated for univalent elements by dividing one faraday by the number of actual ions in the gram equivalent, i.e. the Avogadro Number, viz. 6×10^{23} . The result obtained for the charge per ion was 1.6×10^{-19} coulombs, and it therefore seemed that this was indeed the magnitude of the unit or "atom" of electricity. Stoney named this unit *the electron*.

The next advance followed the discovery by Sir William Crookes (1879) that gases which under normal conditions are good insulators can be made equally good conductors of electricity by considerably reducing their pressure. Some twenty years later Sir J. J. Thomson (1897) made his famous observation that at extremely low pressures—of the order of one-hundredth of one millimetre of mercury—the current is carried through a gas by *cathode rays*. These rays were shown to travel in straight lines normal to the cathode, to possess mass, and therefore, when moving, momentum, and to be capable of deflection by both electric and magnetic fields; they appeared to consist of negatively charged particles of mass $1/1836$ of that of the hydrogen atom and with a negative charge of 1×10^{-19} coulombs. It is to these particles which, since they can be produced by a great variety of methods, e.g. electric discharge in high vacua, by the action of ultra-violet light on

metals, in flames, from heated wires, by the action of X-rays, and from radioactive substances, appear to be constituents of all matter, that the name electron is now applied.

The Proton. The discovery of the electron was followed by a search for its positive counterpart. It was by using a vacuum tube fitted with a perforated cathode (Fig. 1) that Sir J. J. Thomson was able to obtain evidence for the existence of positive rays and to show that these too seemed to consist of moving particles. He found that for these particles the ratio of charge to mass (e/m) was not constant as it had been for electrons but depended on the nature of the gas present in the

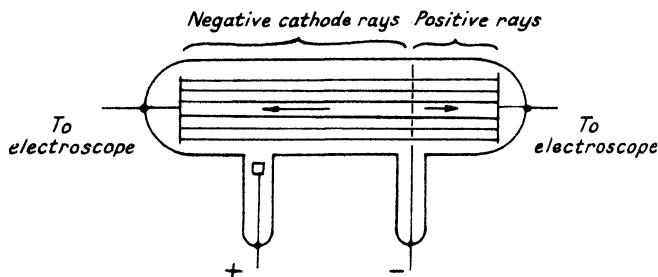


FIG. 1.—Cathode Ray Tube.

tube. The mass of the positive particle was shown to be virtually the same as that of the atom from which it was derived. Hence it appeared that when a gas is ionised one or more electrons of negligible mass are expelled from some of its atoms, leaving positively charged particles behind. The *simplest* of all positive particles was obtained when highly evacuated hydrogen filled the discharge tube, and this particle, with weight 1.007 ($0=16$) and a positive charge of magnitude equal to that of the electron, 1.6×10^{-19} coulombs, was called a *proton*.

The Atom. The conclusion drawn from this and other work was that chemical atoms, which are, of course, normally electrically neutral, are composed of protons and an equal number of electrons. Ideas, however, on the actual ways in

which these were arranged inside the atom were not at that stage particularly clear.

A number of theories of atomic structure were subsequently put forward and the most fruitful was that proposed by Sir Ernest Rutherford in 1911—the theory of the nuclear atom. This theory was based on the fact that when α -particles (which are emitted by radioactive substances like radium and have been shown to consist of helium atoms carrying two unit positive charges) are directed towards thin metal foil most of them pass straight through but an exceedingly small proportion (about 1 in 20,000) are deflected through quite large angles. Rutherford therefore assumed that the whole of the positive charge in an atom is concentrated in a minute nucleus, which is surrounded, at a relatively large distance, by the equivalent negative electrons. Measurements of the angle of scattering of the α -particles enabled calculations to be made which resulted in the pertinent suggestion that the number of positive charges on the nucleus of an atom is the same as the ordinal number of the particular element in the periodic table, which was subsequently called its atomic number (Z).

Atomic Number. During the work on cathode rays it was discovered that when they impinge on a target (anticathode) an extremely penetrating form of radiation of very short wavelength, known as X-rays, is produced. H. G. J. Moseley, in 1913, examined the X-rays emitted by anticathodes which either consisted of, or were coated with compounds of, various elements. By using a crystal of potassium ferrocyanide as a diffraction grating he was able to obtain photographs of the characteristic X-ray spectra for the elements from aluminium ($Z=13$) to gold ($Z=79$). Each of the elements gave a series of lines (identified as the K, L, M lines respectively) and Moseley calculated the frequency of the X-ray producing each of these lines for the elements examined. He was able to show that a definite relationship existed between the frequency of, e.g., the characteristic K-line and the atomic number. This took the

form $\nu = a(Z - b)^2$, where a and b are constants. Thus, when the square root of the frequency is plotted against the atomic number the graph obtained is a straight line (Fig. 2). It thus appeared that the ordinal number, i.e. the atomic number, had a definite and fundamental significance. Moseley was the first to be able to limit the number of elements between hydrogen and uranium to 92, to indicate the number of missing elements and to explain the underlying reason for the correct placing of the heavier elements argon, cobalt and tellurium

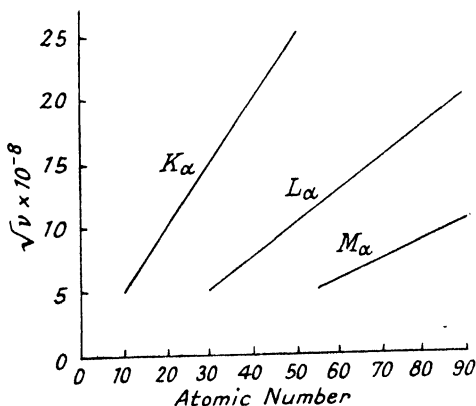


FIG. 2.—Relationship between Characteristic Frequency and Atomic Number.

before the respectively lighter potassium, nickel and iodine in the periodic table. The fundamental conclusion cannot better be stated than in Moseley's own words : " There is in the atom a fundamental property which increases by regular steps as we pass from one atom to the next. This quantity can only be the charge on the positive nucleus." An element of atomic weight W and atomic number Z will therefore have a nucleus with a positive charge Z surrounded by Z electrons. It was once thought that such a nucleus would consist of W protons and $W - Z$ electrons with a net positive charge of Z , but it is now believed to contain Z protons and $W - Z$ neutrons, thus

having a total mass of W and a positive charge of Z . Neutrons are particles of unit mass and no electric charge and were discovered by J. Chadwick in 1932.

Electron Orbits. The first attempt to solve the problem of the arrangement of the electrons around the nucleus was made by Sir Ernest Rutherford when he suggested that the electrons revolve round the nucleus like the planets revolve round the sun. Neils Bohr pointed out, however, that the number of orbits available for these electrons must be limited and that the electrons could only rotate in orbits in which they possess definite discrete amounts or quanta of energy; thus the only orbits available would be those in which the electrons have one, two, three, four, . . . etc., quanta of energy.

It was at first assumed that the electron orbits were circular, but Sommerfeld showed that they could be elliptical and that two quantum numbers would then be needed—one to express the major axis of the ellipse and the other to indicate its minor axis. It was later found that two more quantum numbers were required, making four in all, in order to describe fully the condition of any one extra-nuclear electron. The actual arrangement of the planetary electrons has been deduced in two ways, the one involving physical measurements and the other an examination of the chemical properties of the elements and their compounds. Both methods lead to practically the same conclusions, and since the latter method, largely developed by Main-Smith (1924), needs little in the way of mathematical treatment, its main arguments may be briefly discussed here.

The Periodic Table. Numerous attempts had been made to classify the elements in such a way that those with similar chemical properties are grouped together in order of increasing atomic weight, but it was not until 1869 that success was achieved by Mendeléeff.

The periodic nature of the chemical and physical properties of the elements, when arranged in order of what is now known as increasing atomic number, is best shown in the form of the

well-established periodic table. This, in modified forms arranged to suit the present argument, is given in Tables I and II below.

TABLE I.—SIMPLIFIED PERIODIC TABLE

		Alkaline		Amphoteric		Non-Alkaline and Acid			
Group :		I	II	III	IV	V	VI	VII	VIII
Period	1	(1H)						1H	2He
	2	3Li	4Be	5B	6C	7N	8O	9F	10Ne
	3	11Na	12Mg	13Al	14Si	15P	16S	17Cl	18Ar
	4	19K	20Ca*	31Ga	32Ge	33As	34Se	35Br	36Kr
	5	37Rb	38Sr**	49In	50Sn	51Sb	52Te	53I	54Xe
	6	55Cs	56Ba***	81Tl	82Pb	83Bi	84Po	85—	86Rn
	7	87—	88Ra						

* 10 elements, 21Sc to 30Zn

** 10 elements, 39Y to 48Cd

*** 24 elements, 57La to 80Hg

The following observations may be made with regard to the arrangement of elements in Table I :

Period 1 includes only two elements, hydrogen, H, which is typical of all chemically active elements, and helium, He, which is the prototype of all the chemically inert elements.

Period 2 includes eight elements, from alkali metal lithium, Li, to inert gas neon, Ne.

Period 3 includes eight elements, from alkali metal sodium, Na, to inert gas argon, Ar.

Period 4 includes eighteen elements, eight as before from alkali metal potassium, K, to inert gas krypton, Kr, with ten elements inserted between calcium, Ca, and gallium, Ga.

Period 5 includes eighteen elements, eight as before from alkali metal rubidium, Rb, to inert gas xenon, Xe, with ten elements inserted between strontium, Sr, and indium, In.

Period 6 includes thirty-two elements, eight as before from alkali metal caesium, Cs, to inert gas radon, Rn, with twenty-four elements inserted between barium, Ba, and thallium, Tl.

Period 7 includes six elements only, two as in first two of previous groups of eight, and the rest inserted after radium, Ra.

It should be particularly noted that there are in each horizontal period *two* alkaline elements, *two* amphoteric elements and *four* non-alkaline elements, the first three of the latter giving rise to acids and the fourth being inert. All of the non-metals, incidentally, fall to the right of an oblique line drawn from boron (5) to eka-iodine (85).

The elements generally known as the *transitional elements* have not yet been included in the table previously discussed; they are therefore given in Table II below.

TABLE II.—PERIODIC ARRANGEMENT OF TRANSITIONAL SERIES ELEMENTS

		High Natural Valency				Low Natural Valency					
Group :		III	IV	V	VI	VII	VIII			I	II
Period	4	21Sc	22Ti	23V	24Cr	25Mn	26Fe	27Co	28Ni	29Cu	30Zn
„	5	39Y	40Zr	41Cb	42Mo	43Ma	44Ru	45Rh	46Pd	47Ag	48Cd
„	6	57La*	72Hf	73Ta	74W	75Re	76Os	77Ir	78Pt	79Au	80Hg
„	7	89Ac	90Th	91Pa	92U						

* 14 rare-earth elements, 58Ce to 71La.

It should be noted the transitional elements in each period of Table II (10 elements) can be divided into two sub-groups, one of *four* elements with high natural valency and the other of *six* elements with low natural valency, i.e. six elements which display low valencies in their naturally occurring compounds.

The fourteen rare-earth elements cannot be arranged in periodic order since they are nearly all trivalent and do not therefore show a regular change of valency in passing from one element to the next. It might be pointed out that all the other elements have one valency in accordance with their positions in the periodic table. However, the rare earths are divisible on

chemical grounds into two sub-groups, one—the cerium earth group—containing *six* elements, and the other—the lutecium earth group—containing *eight* elements.

Hydrogen and Helium. A consideration of the arrangements of the elements in the periodic table has shown that if the transition and rare-earth elements are for the moment neglected there is a definite periodicity of chemical and physical properties, and, presumably, of atomic structure, with every group of eight elements. This periodicity starts at Li (Atomic Number 3), which follows H(1), the first of all valent elements, and He(2), the first inert element. There are strong reasons for believing that chemical activity is associated with incomplete layers of extra-nuclear electrons, and it thus seems that the first layer is capable of holding two electrons, being incomplete with one electron in the hydrogen atom and complete with two in inert helium. The extra-nuclear electrons in these two elements can be indicated as follows *: H 1 ; He 2.

The Second and Third Period Elements. The second period contains eight elements and includes the two alkali metals Li(3) and Be(4), the two amphoteric elements B(5) and C(6), and the four non-alkali elements N(7), O(8), F(9) and Ne(10). It would thus seem that the electrons of the inert neon atom are arranged in two complete layers, the *first* layer consisting of *two* electrons, as in the helium atom, and the *second* layer containing *eight* electrons, arranged in sub-groups of two, two and four. Thus the electron structures of the second-period elements are as follows: Li 2.1, Be 2.2, B 2.2,1, C 2.2,2, N 2.2,2,1, O 2.2,2,2, F 2.2,2,3, and Ne 2.2,2,4; the electrons of the second and outer layer have been underlined in order to distinguish them from the first and inner layer of two.

In the *third* period we find the building up of a *third outer layer* of electrons which is completed at the inert argon, the

* The notation here is as follows: He (2) means the element helium, atomic number two, while He 2 indicates that the helium atom has two extra-nuclear electrons.

total number of additional electrons needed being eight and their arrangement being in groups of two, two and four as before. The extra-nuclear electrons of the third period are therefore as follows: 11Na 2.2,2,4,1, 12Mg 2.2,2,4,2, 13Al 2.2,2,4,2,1, 14Si 2.2,2,4,2,2, 15P 2.2,2,4,2,2,1, 16S 2.2,2,4,2,2,2, 17Cl 2.2,2,4,2,2,3, and 18A 2.2,2,4,2,2,4. (The third and outer layer electrons have in this case been underlined.)

The Fourth Period Elements. Coming to the fourth period we find that the first two elements, potassium and calcium, resemble, respectively, the first two elements of both preceding periods, and, if the ten transition elements from scandium to zinc are excluded, the period is completed at the "eighth" element, inert krypton. It would therefore seem that the *fourth* electron layer resembles the preceding ones in that it *may* contain *eight* electrons, in sub-groups of two, two and four. If this is so then the additional *ten* electrons of the transitional elements must in their atoms find accommodation in the *third* and immediate inner layer. It will be remembered that these ten elements form sub-periods of four with high natural valency and of six with low natural valency, which suggests that the electrons which have to join the third layer do so by the building up there of additional sub-groups of four and six electrons. Thus we have the following for the electron architecture of the fourth period :

19K	<u>2.2,2,4,2,2,4,1</u>	28Ni	<u>2.2,2,4,2,2,4,4,4,2</u>
20Ca	<u>2.2,2,4,2,2,4,2</u>	29Cu	<u>2.2,2,4,2,2,4,4,6,1</u>
21Sc	<u>2.2,2,4,2,2,4,1,0,2</u>	30Zn	<u>2.2,2,4,2,2,4,4,6,2</u>
22Ti	<u>2.2,2,4,2,2,4,2,0,2</u>	31Ga	<u>2.2,2,4,2,2,4,4,6,2,1</u>
23V	<u>2.2,2,4,2,2,4,3,0,2</u>	32Ge	<u>2.2,2,4,2,2,4,4,6,2,2</u>
24Cr	<u>2.2,2,4,2,2,4,4,1,1</u>	33As	<u>2.2,2,4,2,2,4,4,6,2,2,1</u>
25Mn	<u>2.2,2,4,2,2,4,4,1,2</u>	34Se	<u>2.2,2,4,2,2,4,4,6,2,2,2</u>
26Fe	<u>2.2,2,4,2,2,4,4,2,2*</u>	35Br	<u>2.2,2,4,2,2,4,4,6,2,2,3</u>
27Co	<u>2.2,2,4,2,2,4,4,3,2</u>	36Kr	<u>2.2,2,4,2,2,4,4,6,2,2,4</u>

* Vide p. 112 for structure deduced by physical methods.

It should be noted that none of the ten elements of the first series of transition elements has more than two outer electrons, and this confirms the idea that the ten more firmly bound electrons can be accommodated in the third group or layer. By the time copper is reached the third layer is complete, leaving only one electron in the outer layer (i.e. the fourth layer), so making the fundamental valency of copper one.

The Fifth Period Elements. The *fifth* period is practically a replica of the fourth, the electrons adding on *at first* to a *fifth* outer layer, capable of holding *eight* electrons, then joining in sub-groups of four and six the *fourth* and nearest inner layer, and finally completing the already started *fifth* outer layer group of eight electrons. Since the similarity to the preceding fourth period is so great it is not thought necessary to give the individual electron architectures in such detail as before; the following are, therefore, the extra-nuclear electron arrangements of atoms of elements of metallurgical interest in the fifth period:

37Rb	2.2,2,4.2,2,4,4,6.2,2,4.1
38Sr	2.2,2,4.2,2,4,4,6.2,2,4. <u>2</u>
39Yt	2.2,2,4.2,2,4,4,6.2,2,4,1,0. <u>2</u>
42Mo	2.2,2,4.2,2,4,4,6.2,2,4,4,1. <u>1</u>
46Pd	2.2,2,4.2,2,4,4,6.2,2,4,4,6.0
47Ag	2.2,2,4.2,2,4,4,6.2,2,4,4,6. <u>1</u>
48Cd	2.2,2,4.2,2,4,4,6.2,2,4,4,6. <u>2</u>
50Sn	2.2,2,4.2,2,4,4,6.2,2,4,4,6. <u>2</u> , <u>2</u>
51Sb	2.2,2,4.2,2,4,4,6.2,2,4,4,6. <u>2</u> , <u>2</u> , <u>1</u>
54Xe	2.2,2,4.2,2,4,4,6.2,2,4,4,6. <u>2</u> , <u>2</u> , <u>2</u> , <u>4</u>

The Sixth Period Elements. The *sixth* period includes, in addition to the ten transition elements, the fourteen "rare earths." It might be expected that the atomic structure develops, as far as the transition elements are concerned, in the same way as it did for their predecessors, the *ten* electrons forming additional sub-groups of four and six in the *fifth*

electron layer. The electrons of the remaining *fourteen* rare-earth elements—which are naturally grouped into six and eight—can then only be included as sub-groups of six and eight electrons in the next but one inner layer, i.e. the *fourth layer*. The following are electron structures of typical sixth period atoms :

55Cs	2.2,2,4.2,2,4,4,6.2,2,4,4,6,0,0.2,2,4, <u>1</u>
56Ba	2.2,2,4.2,2,4,4,6.2,2,4,4,6,0,0.2,2,4, <u>2</u>
57La	2.2,2,4.2,2,4,4,6.2,2,4,4,6,0,0.2,2,4,1,0, <u>2</u>
58Ce	2.2,2,4.2,2,4,4,6.2,2,4,4,6,1,0.2,2,4,1,0, <u>2</u>
71Lu	2.2,2,4.2,2,4,4,6.2,2,4,4,6,6,8.2,2,4,1,0, <u>2</u>
74W	2.2,2,4.2,2,4,4,6.2,2,4,4,6,6,8.2,2,4,4,0, <u>2</u>
78Pt	2.2,2,4.2,2,4,4,6.2,2,4,4,6,6,8.2,2,4,4,4, <u>2</u>
79Au	2.2,2,4.2,2,4,4,6.2,2,4,4,6,6,8.2,2,4,4,6, <u>1</u>
82Pb	2.2,2,4.2,2,4,4,6.2,2,4,4,6,6,8.2,2,4,4,6, <u>2,2</u>
83Bi	2.2,2,4.2,2,4,4,6.2,2,4,4,6,6,8.2,2,4,4,6, <u>2,2,1</u>
86Rn	2.2,2,4.2,2,4,4,6.2,2,4,4,6,6,8.2,2,4,4,6, <u>2,2,4</u>

The Seventh Period Elements. The remaining six places in the *seventh* and last period are filled with atoms which, apart from their pronounced radio-active properties, introduce nothing new in the way of electron arrangement. The first two elements, eka-cæsium and radium, have respectively one and two electrons in a new *seventh* outer layer, while the four remaining elements fall in line with the first four transition elements of periods four and five. It would thus seem that the four electrons concerned then take their places in the *sixth* layer, the outer two persisting in the last four of the known elements. Thus :

88Ra	2.2,2,4.2,2,4,4,6.2,2,4,4,6,6,8.2,2,4,4,6.2,2,4, <u>2</u>
92U	2.2,2,4.2,2,4,4,6.2,2,4,4,6,6,8.2,2,4,4,6.2,2,4,4,0, <u>2</u>

CHAPTER II

ATOMS IN METALS AND ATOMS IN MOLECULES

From ordered arrangement of Elements to ordered arrangement of Alloys. It has been shown that the periodic table, in that it arranges elements in groups with similar chemical properties, has brought order into what must at one time have seemed the disorder of inorganic chemistry. Further, the periodic change of properties of the elements with increase of atomic number has been used to develop the ideas on atomic structure which are now generally accepted as giving a reasonably accurate mental picture of the actual state of affairs inside the individual atoms. Thus, the accumulation of a vast amount of information on chemical and other properties has been condensed into a fairly simple and concise table which has not only enabled the chemist to inter-relate his elements but has resulted in his being able to predict the physical structures of the atoms of which those elements consist.

As far as the physical metallurgist is concerned there is also available to him a great deal of more or less accurate information on the properties and structures of alloys in the form of the numerous equilibrium or constitutional diagrams, which themselves condense the results of the many investigations which have been carried out by previous workers. Until quite recently, however, these structure-summarising diagrams showed little in the way of order or inter-relationship and the different alloy systems seemed to be as disconnected as the chemical elements must have appeared before the advent of the periodic table. Recent work has altered this state of affairs and order is beginning to appear; strangely enough, the correlation of the structural relationships for the apparently different alloy systems owes much to its chemical predecessor—

the periodic table. It must be pointed out that considerably more than that is involved in the modern study of alloy structures. It might be said that the most important recent advances are due to the results of X-ray examination combined with the application of the electronic theory, both of atom structure and size and of inter-atomic forces in chemical compounds and metal crystals. Indeed, as Hume-Rothery says: "The . . . metallurgist of the future will inevitably have to acquire the habit of thinking in terms of atomic and electronic ratios, just as the chemist automatically thinks of sulphuric acid as H_2SO_4 and not as a ternary compound of hydrogen, sulphur and oxygen containing 2.04, 32.65, and 65.31 percentage by weight of these elements respectively."

Factors which determine Structures of Alloys. It might be as well at this stage to make the definite statement that the types of alloy structure formed by a binary system seem to depend on the following tendencies of the two metals concerned:

- (a) The tendency to form solid solutions, which usually are of the substitutional type; and
- (b) the tendency to form hard, brittle intermetallic compounds.

It will be shown that, in general, these tendencies work in opposition to each other, and the type of equilibrium diagram for a given alloy system is largely determined by which of the two is the predominating force. It would appear fairly obvious that the formation of substitution solid solutions would be favoured by, among other things, a similarity in size of the atoms concerned, while the governing factor in the production of intermetallic compounds would depend, with the same qualification, on the possibility of the development of inter-atomic forces of the nature of those found in other compounds. The determination of the size of the atom with accuracy offers some difficulty, particularly in view of the fact that for many purposes it is convenient to regard an atom as not having a sharp boundary, but as consisting of a positively charged nucleus surrounded by a cloud of negative electricity, the cloud being formed by the electrons

in the various quantum layers or shells. Again, the question of the size of the atom involves a discussion of the results of the X-ray examination of metal and other crystals. It will, therefore, be convenient to deal with this point later and to pass on to the electronic theory of chemical combination or the electronic theory of valency, which amounts to the same thing. This is, of course, an ever-widening subject, and we must for the moment content ourselves with only the briefest outline of this recent and fundamental advance of chemistry.

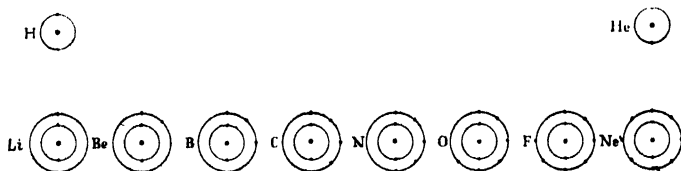
Valency. The principles of the electronic theory of valency may be summarised as follows :

(a) The driving force of chemical combination is the marked tendency for the outer shell of the extra-nuclear electrons to attain the number of electrons found in the outer shell of the nearest inert gas in the periodic table.

(b) The completion of this stable outer shell may be brought about either by the complete transference of the extra outer electrons of one atom to another atom needing just that number to complete its own outer shell, or by the sharing of the outer electrons of two atoms in such a way that they both attain, as a result of the sharing, a stable outer group of eight electrons, as in the inert gas atoms.

The first of these two principles needs little in the way of further comment, and we shall therefore proceed to discuss the latter in rather more detail. For this purpose it is convenient to picture the atoms of the early periods as shown in Table III, in which the larger dots represent the nuclei and the smaller ones the extra-nuclear electrons.

TABLE III.—EXTRA-NUCLEAR ELECTRONS OF FIRST TEN ELEMENTS



Since it is only the outer shell of electrons which is involved in chemical combination the necessary data may be expressed in a simplified form in which attention is concentrated only on the particular electrons—the valency electrons—involved in such combination. The valency electrons of the elements of the second and third periods may then be shown as in Table IV.

TABLE IV.—EXTRA-NUCLEAR ELECTRON NOTATION—SECOND AND THIRD PERIODS

Li	Be	B ·	·C:	·N:	·O:	·F:	:Ne:
Na	Mg	Al ·	·Si:	·P:	·S:	·Cl:	:Ar:

Electrovalency. The two types of chemical combination may now be discussed. The first, in which complete transference of electrons from one atom to another takes place, is known as electrovalency, for, with the completion of the stable electron arrangement of the one atom at the expense of the other, both atoms are left in the form of *charged ions which are then held together by electrostatic attraction*, whether in the solid or liquid states. Thus, for example, the combination of atoms of sodium, possessing one electron in excess of an inert gas structure, and chlorine, with one electron short of the structure of argon, may be visualised as follows: $\text{Na} \cdot + \cdot \ddot{\text{Cl}}: \rightarrow (\text{Na})^+(\text{Cl})^-$. This type of combination takes place only when the number of electrons transferred is *small*; thus Na can form $(\text{Na})^+$ and Mg can give $(\text{Mg})^{++}$ ions, but we never encounter ions of the type $(:\ddot{\text{Na}}:)^{7-}$, $(:\ddot{\text{Mg}}:)^{6-}$, or even $(\text{C})^{4+}$ or $(:\ddot{\text{C}}:)^{4-}$. The complete transfer from one atom (or to an atom) of a *large* number of electrons would produce an *extremely unstable ion*.

Covalency. The second type of chemical combination takes place by the sharing rather than the transference of electrons, and this results in combination by what is termed covalency.

It is thus possible, e.g., for two chlorine atoms to combine and form a molecule by each atom sharing one of the electrons belonging to the other ; $\cdot\ddot{\text{Cl}}\cdot + \cdot\ddot{\text{Cl}}\cdot \rightarrow :\ddot{\text{Cl}}:\ddot{\text{Cl}}:$. A similar mechanism accounts for the formation of molecules of nitrogen, carbon dioxide, etc., as follows ; $:\text{N}^{\cdot\cdot} + :\text{N}^{\cdot\cdot} \rightarrow :\text{N}^{\cdot\cdot}:\text{N}^{\cdot\cdot}:$ and $:\ddot{\text{O}} + :\text{C}: + \ddot{\text{O}} \rightarrow :\ddot{\text{O}}:\text{C}:\ddot{\text{O}}:$. It will be noticed that covalency is responsible for the combination of atoms with comparatively large numbers of valency electrons, i.e. atoms of elements falling on the right-hand side of the periodic table. In these cases the elements are bound together in such a way that there is * no resultant inter-atomic electrostatic force, so that covalent compounds are unable to undergo ionisation and are therefore quite distinct from electrovalent ones.

* It should be mentioned that there are, in fact, a number of covalent compounds, of which water is a well-known example, in the molecule of which there *is* a resultant interatomic electrostatic force. These forces are thought to be due to *uneven* sharing of electrons and they are responsible for the existence of dipole moments. Such forces are of considerable importance in the modern electronic theories of organic chemistry, but from our present viewpoint they need no further consideration.

CHAPTER III

ATOMS IN CRYSTALS

Ionic and Homopolar Linking of Atoms. We have seen how different atoms may combine in at least two ways—either by means of complete electron transference (*electrovalency*), producing an *ionic* bond *; or by means of electron sharing (*covalency*), in which case the linkage produced is said to be *homopolar*. Both of these types of binding produce high interatomic attractive forces, and it is interesting to note that the actual forces are of the same order of magnitude although their mechanisms are so fundamentally different.

Valency Electrons in Metal Crystals. When we come to deal with solid metals the position is very different. An examination of the electronic structure of metal atoms shows that in all cases the number of outer-layer extra-nuclear electrons is small, rarely exceeding two, and more rarely still exceeding three. There are good reasons for believing that in solid metals the atoms give way to their normal tendency to lose their outer electrons and thus form positively charged ions. The electrons so liberated have to take up their positions between these ions, and since the interatomic distances are very small, the electrons themselves are in turn so near the individual positive ions that the attractive forces between, for example, one valency electron and its many neighbouring ions will all be of the same order of magnitude. Thus, such a valency electron may be said to belong to no one positive ion in particular, but to belong to the positive ions as a group. It may indeed be said that in solid metals the valency electrons form a sort of paste holding the positive ions together; this “paste”

* Sometimes known as a “polar” bond.

is, however, still fluid enough to be able, under a suitable driving force, to flow round the metal ions.

Valency Electrons and Electrical Conductivity of Metals. At very low temperatures, when the natural vibration* of the ions is near its minimum, very little resistance is offered to the flow of electrons—i.e. to the flow of an electric current. However, as the temperature rises, the natural vibration of the ions increases, and this hinders electron flow. It is for these reasons that the electrical resistance of metals is low compared with that of other materials and that it increases with rise of temperature in accordance with the well-known equation $R_t = R_0(1 + \alpha t + \beta t^2)$, where R_t = resistance (in ohms) at temperature $t^\circ \text{C.}$, R_0 = resistance at 0°C. and α and β are constants.

When the atoms of a solid are joined by either ionic (electron transfer) or homopolar (electron sharing) forces the crystals have no “free” electrons. Such solids, e.g. sodium chloride and diamond, are either very poor electrical conductors or insulators. It is, of course, well known that sodium chloride and other similar ionic salts, when in the fused condition, are good electrical conductors; it must be remembered, however, that under these conditions they owe their conducting powers to the presence of comparatively *free ions*, and it is these ions which actually transport the current.

While discussing electrical conductivity, it is of interest to refer to the electronic structures of silver and copper, the best and second-best, respectively, of all electrical conductors. We have already shown (pp. 17 and 18) that the extra-nuclear electron structures are: Cu 2,8,18,1 and Ag 2,8,18,18,1. The inner shells are virtually complete and each atom is readily able to detach its one valency electron; hence their extremely good conductivity. Further, in the case of the silver atom the valency electron is in the fifth shell while that of the copper

* Atoms, or ions, in solids, are not *fixed* in space. They vibrate about fixed points, and the higher the temperature the greater is the intensity of this vibration.

atom is in the fourth shell ; in other words, the valency electron of the silver atom is further from the positive nucleus than is the corresponding electron of the copper atom. The outer electron is therefore more easily detached in silver than in copper, and this explains the rather better electrical conductivity of the former metal. It is a surprising fact that the alloying of a small amount of silver with copper actually *reduces* the electrical conductivity under conditions when it would be expected to increase it ; our study of the nature of solid solution type alloys may help to explain this apparent anomaly.

The Residual Force Bond. We have now accounted for three types of atomic linkage known respectively as the ionic, the homopolar and the "metallic" types. It should be mentioned, however, that there is yet a fourth type of interatomic attraction. This is the force which comes into play when even the atoms of the inert gases are held together as they are when these gases are liquified, or, even more so, when they are solidified. The forces then brought into play may be described as "residual forces," and it is they that are involved in the building up of crystals of organic compounds like, for example, those present in paraffin wax. The organic compound—in this case a hydrocarbon—is built up of atoms of various elements held together in the molecule by homopolar forces ; the crystals themselves are composed of these molecules, and the molecules in turn are united by means of the residual forces.

Crystal Types. Crystals can, therefore, be classified in four groups, as follows : (A) Ionic Crystals, (B) Homopolar Crystals, (C) Metallic Crystals and (D) Residual Force Crystals ; these are typified respectively by crystals of sodium chloride, diamond, iron and paraffin wax. We shall, in the present work, naturally be concerned mainly with metallic crystals and will have to deal in some detail with their individual structures. It might not, however, be out of place to include here the following brief summary of the properties which characterise the different crystal types. This may be done as follows :

(A) *Ionic Crystals*. These are transparent, have high melting-points (e.g. sodium chloride melts at 801°C.), have very low electrical conductivity, and are hard, elastic under tension but brittle under impact.

(B) *Homopolar Crystals*. Such crystals also are transparent and tend to have high melting-points. They do not conduct electricity. They are extremely hard—the diamond, for example, being the hardest substance known—and are extremely brittle. They cannot undergo plastic deformation.

(C) *Metallic Crystals*. These crystals are opaque to light. They are good conductors of electricity and have relatively high melting-points. These crystals are by comparison soft and can undergo plastic deformation to a considerable extent by gliding along cleavage planes. They are for this reason usually far from brittle.

(D) *Residual Force Crystals*. Crystals of this type are transparent. They have very low melting-points and are electrical insulators. As far as mechanical properties are concerned, these crystals are soft, weak and plastic.

It must be pointed out that these generalisations must not, of course, be expected to be capable of fitting in with all the properties of the numerous individual crystals. Some crystals, in fact, show some of the properties of one group and some of another. In fact, the structure classification must not itself be applied with too great rigidity, since there are crystals in which there appear to be two types of interatomic attraction acting at the same time. For classification purposes the scheme has considerable value and the student should obtain much in the way of mental exercise by trying for himself to explain the various properties of the different crystal types, with reference to the previously established crystal-building forces actually functioning in those individual crystals given as typical examples.

Electron Energy Zones in Metal Crystals. Before leaving the subject of the nature of the binding forces in crystals it might

be mentioned that there are reasons for believing that a metal crystal, consisting as it does of ions and electrons, may be regarded as a huge molecule in which the electrons occupy a whole series of energy states somewhat similar to those found in the free atom. The modern theories of W. Hume-Rothery and H. Jones are based on the assumption that these states are divided into different groups known as the Brillouin Zones. In a normal metal these zones overlap, so that comparative freedom of motion is offered to the valency electrons and the metal has good electrical conductivity. Hence, in Hume-Rothery's own words, "we are led to expect relations between crystal structures, phase boundaries in equilibrium diagrams, and the number of valency electrons per unit cell, and hence the ratio of valency electrons to atoms."

X-Rays and X-Ray Diffraction. Although a great deal of information had been accumulated as a result of the study of the external forms of crystals, it was not until 1912, when von Laue suggested that a crystal might act as a diffraction grating for X-rays, that the first real advance was made in the examination of the actual arrangement of atoms *inside* crystals. We have already seen how X-rays are emitted when a metal target or anticathode is bombarded with a stream of electrons (p. 11). These rays have been shown to be a form of radiation similar in nature to those of radio and light and differing from them only in wavelength and penetrating properties. Thus, the radiation produced by a short-wave radio transmitter may have a wavelength of ten metres while that of ordinary light has a wavelength of the order of one hundred thousandth of a centimetre; X-rays are of extremely short wavelength, the actual figure being usually less than one hundred millionth of a centimetre.

It may easily be demonstrated that ordinary white light is composed of a number of lights of different colours—i.e. of different wavelengths—by producing a spectrum, either by means of a prism or of a diffraction grating. A diffraction grating consists of a number of parallel lines ruled on a sheet of

glass—the distance between these lines being of the order of one-fifth of a “tenth of a thou. . . .” (2×10^{-5} inches). If a beam of light of a definite colour, i.e. monochromatic light, is directed on to a suitable diffraction grating each space between the lines becomes the centre of a new train of waves, as shown in Fig. 3. In the directions in which the new waves are in step, or in phase, the light will continue to pass, but there will be no light emerging in those directions in which the waves are out of phase. A diffraction grating is thus able to deflect a beam of

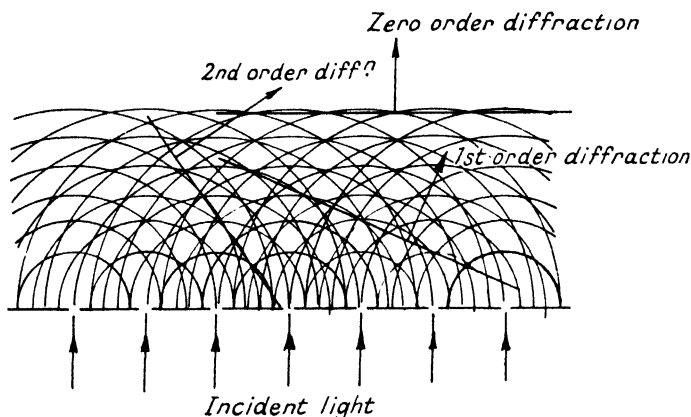


FIG. 3.—Diffraction of Wave Motion.

incident monochromatic light through definite angles, producing first order, second order, third order, etc., diffracted beams.

Laue and X-Ray Diffraction. The suggestion made by von Laue was that the distance between the atom planes in crystals should be of the same order as the wavelength of X-rays, so that it should be possible to use a crystal as a diffraction grating for this particular type of radiation. It was by following up this suggestion and using the apparatus shown in outline in Fig. 4 that his associates, Friedrich and

Knipping, were able to obtain the first X-ray diffraction photograph—shown in diagrammatic form as an inset to Fig. 4. It should be mentioned that for work of this type it is best to use monochromatic X-rays, which can be obtained by controlling the voltage, the nature of the anode and anti-cathode of the X-ray tube, and subsequently passing the spectrum of

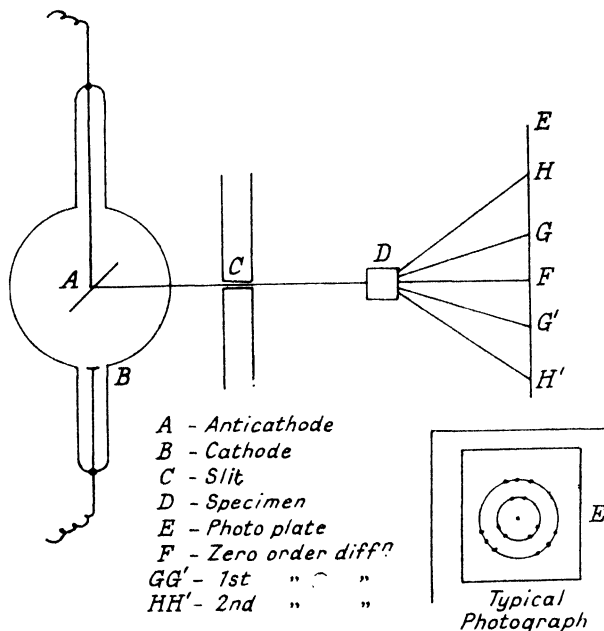


FIG. 4.—Laue Method of X-Ray Diffraction.

X-rays through a suitable filter of solid material. Owing to the difficulties involved in obtaining stress-free single crystals the Laue method is no longer used.

Bragg and X-Ray Reflection. In 1913 Sir William Bragg and his son—now Sir Lawrence Bragg—showed that X-ray diffraction patterns could equally well be explained on a basis of *reflection* from the planes of atoms in the crystal. They were

able to develop what is now known as *Bragg's Law* and which indicates that X-ray reflection will only take place under conditions which are governed by a definite relationship between λ , the wavelength of the X-rays, θ , the angle of incidence of the X-rays, and d , the distance between the reflecting planes of atoms. Thus, if in Fig. 5 AB and CD represent two parallel planes of atoms and EF and GH two parallel X-rays of the same wavelength λ and incident at an angle θ to the atom planes, then FL and HM are the respective reflected rays. The path GHM is longer than the path EFL by a distance equal to JH plus HK, i.e. 2JH. It can be shown that 2JH is equal

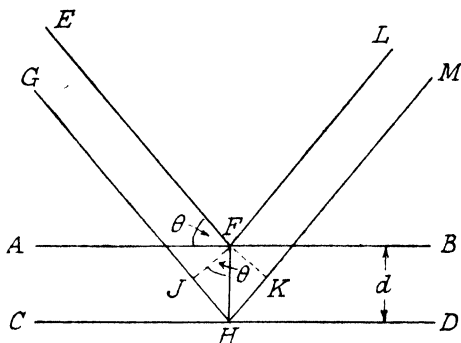


FIG. 5.—Bragg Reflection.

to $2d \cdot \sin \theta$. Hence, in order that the two reflected rays might reinforce each other they must be in phase, and this condition can only be satisfied if the extra distance travelled by the second ray is a whole number of wavelengths. This condition can be expressed as follows: $n\lambda = 2d \cdot \sin \theta$. By using X-rays of a previously determined wavelength it is thus possible, by studying their reflection by crystals, to calculate the distances between the different parallel atom planes and thus determine the atomic arrangements within the crystals.

The general lay-out of the apparatus now used for examining crystals by the Bragg X-ray Reflection Method is shown in

Fig. 6, in which is also included a sketch of a typical reflection photograph obtained with such equipment. It may be pointed out in this connection that the Bragg method is one of the best of those available for the examination of crystal structures.

The "Powder Method" for Metals. A modification of this method which has proved of particular metallurgical interest was developed by Debye and Scherrer in 1916 and by Hull in 1917. These workers showed that X-ray diffraction patterns

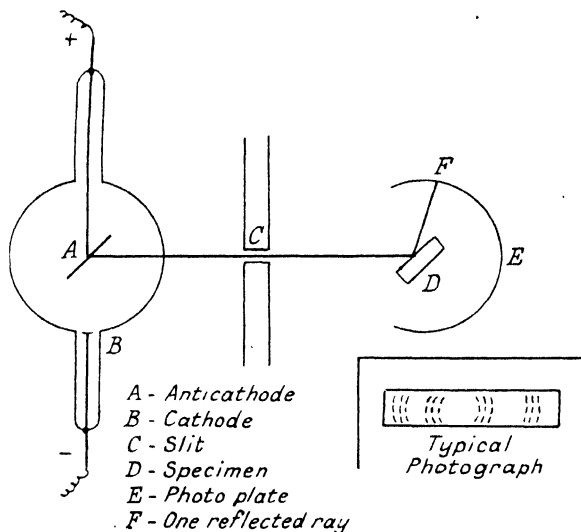


FIG. 6.—Bragg Method of X-Ray Diffraction.

can be produced without using an isolated individual crystal and can be quite satisfactorily obtained with both powders and normal fine-grained metals. The principle involved in the "powder method" of crystal analysis is that in both powdered crystals and fine-grained metals *there will be a proportion of small crystals or crystal grains which will be suitably orientated to reflect the incident rays.* In other words, the reflecting planes of such crystals or grains will naturally be so arranged

that the angle of incidence of the monochromatic X-ray beam will be the same for all of the particular crystals or grains concerned, viz. the fraction with this suitable orientation. It must, however, be emphasised that these individual small reflecting planes will not, under normal conditions, be coplanar, owing to the natural variation in orientation from one grain to the next. They may, in fact, be regarded as forming part

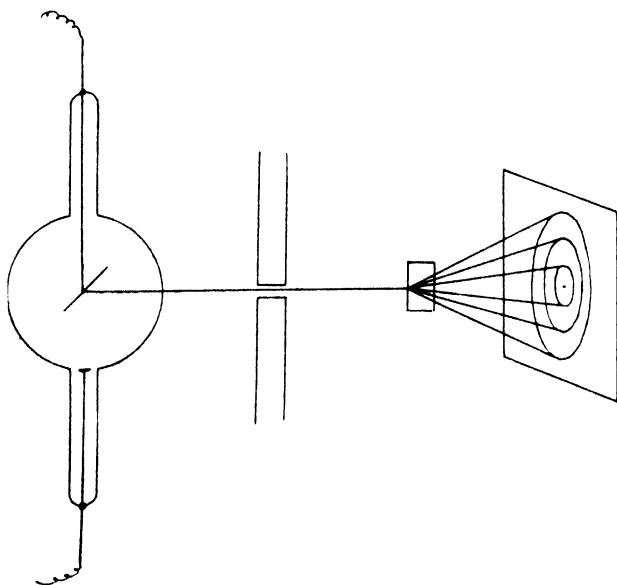


FIG. 7.—Powder Method of X-Ray Diffraction.

of the surfaces of imaginary cones, so that the reflected rays themselves will take the form of cones (of correspondingly larger angles) the intersections of which with a flat photographic plate or film at right angles to the incident beam will be found to produce a series of circles. It is possible, by measuring the diameter of the individual circles, to calculate the positions of the reflecting planes ; in a similar way, the measured

thickness of the ring can be used to deduce the actual grain size, even when the "crystallites" have been produced by severe cold working. The principle of the powder method is

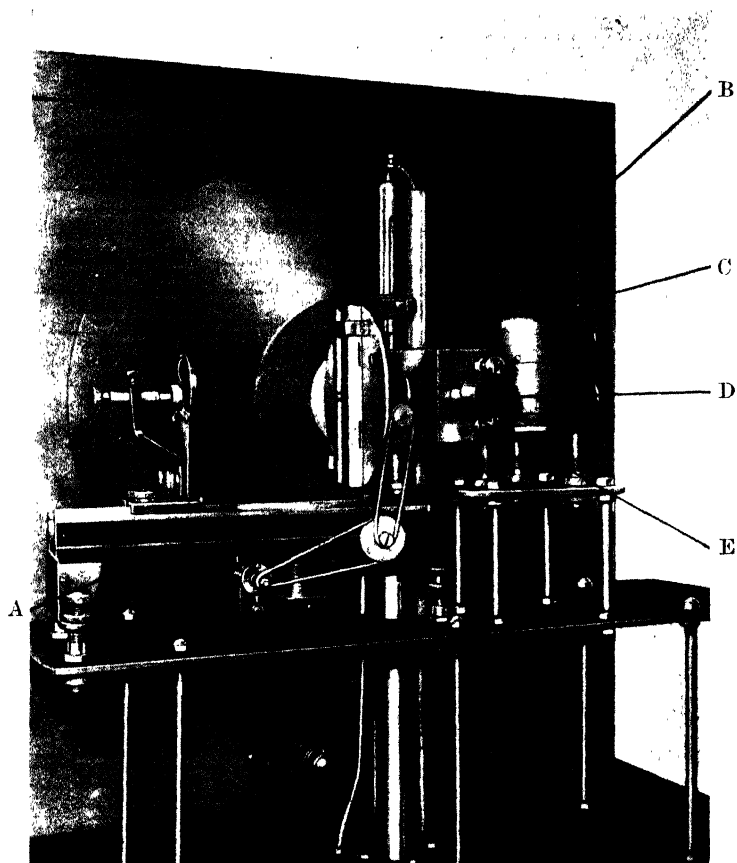


FIG. 8.—Modern X-Ray Diffraction Equipment, Showing Powder Camera and Universal Camera.

A. Universal Camera, B. X-Ray Head, C. 9 cm. Powder Camera, D. Target Assembly, E. Window for X-Rays.

shown in diagrammatic form in Fig. 7, and a typical modern X-ray diffraction apparatus, equipped for powder, back-reflection and transmission X-ray examination methods, is



FIG. 9.—Back Reflection Photograph. Annealed Nickel Sheet.

shown in Fig. 8. An actual back-reflection photograph obtained with this apparatus from annealed sheet nickel is given in Fig. 9.

CHAPTER IV

ATOMS IN METAL CRYSTALS

Space Lattices. X-rays have now been in use for the examination of the internal structure of crystals for some thirty years, and the careful interpretation of the X-ray photographs collected over this period has revealed a great deal of information with regard to the actual arrangement of atoms—or, rather, ions—in the crystal grains of metals. It has been clearly shown that in metal crystals there are only a few general types of regular atomic arrangement, called space lattices. These can easily be derived by imagining that the atoms are packed together *as if* they are spherical in shape; the atoms may not be actually spherical in shape, but when packed together in crystals they seem to behave as though they are of this particular form. This assumption is well justified by results, and we shall proceed to consider the ways in which atom “spheres” may be placed together in order to build up a crystal grain.

The Body-Centred Cubic Lattice. We might start by placing a number of spheres on a horizontal plane so that their centres are at the corners of squares, as shown in Fig. 10 (*a*). It will be noticed that there are gaps between the atom spheres, and that this form of packing is fairly “open” in character as compared with alternative methods which will be discussed later. The second layer of atoms is then placed, as shown by the broken circles, so that their centres lie over the intersections of the diagonals of the squares formed by the centres of the first layer spheres; thus, the second layer spheres rest in contact with four of the spheres of the first layer. The third and fourth, and subsequent, layers are merely repetitions of the first two, so that atoms of the third layer are directly over

those of the first and those of the fourth layer are immediately over those of the second. Thus, a regular space lattice is built up, the unit of which is repeated throughout the crystal grain, and which, with dots to represent atom centres, is shown in Fig. 10 (b). A lattice with this type of unit is known as a body-centred cubic one, and is found, for example, in the metal iron, at ordinary temperatures. It has been shown that the length of the side of the unit cube, or the lattice parameter, of ferrite at ordinary temperatures is 2.86\AA , the symbol \AA representing one Angstrom unit, equal to 10^{-8} cm. ; the cube corner atoms

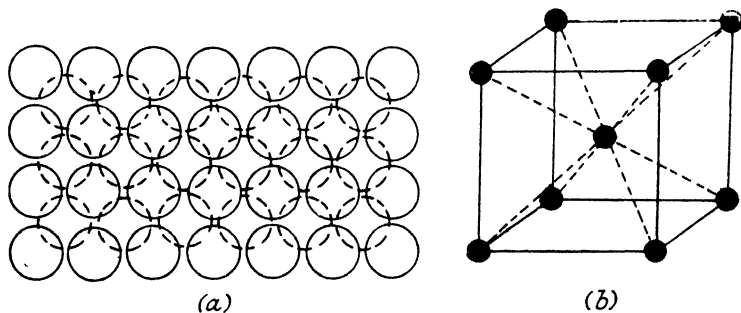


FIG. 10.—(a) Body-Centred Cubic Lattice, Atom Space Model. (b) Body-Centred Cubic Lattice Unit.

are 2.86\AA apart, so that there would be about three and a half millions of them along the side of a 1 mm. cube.

It is interesting to note that there are, in the body-centred cubic lattice unit, nine atoms, of which only one, the centre one, belongs entirely to the lattice unit itself. The eight corner atoms are each in turn shared by eight adjacent unit cubes, so that only one-eighth of each of them really “belongs” to the original unit. The unit therefore contains $1 + 8 \times \frac{1}{8}$ atoms, i.e. 2 atoms. It is thus possible to calculate density from crystal structure data. In the case of a body-centred cubic metal it can be seen that

$$\text{Density} = \frac{\text{Weight of atoms in cube}}{\text{Volume of cube}}$$

$$= \frac{\text{Weight of hydrogen atom} \times \text{Atomic weight of metal} \times 2}{\text{Volume of cube}}.$$

This equation may be applied to body-centred cubic α -iron :

$$\text{Density} = \frac{1.662 \times 10^{-24} \times 55.85 \times 2}{(2.86 \times 10^{-8})^3} = \frac{1.662 \times 55.85 \times 2}{23.4} = 7.94.$$

It might be noted that it is even possible for such a calculation to give a more accurate figure for density than that measured by ordinary methods.

The Close-Packed Hexagonal Lattice. The body-centred cubic lattice is not the only type of lattice which can be produced by the placing together of spheres. There are two other

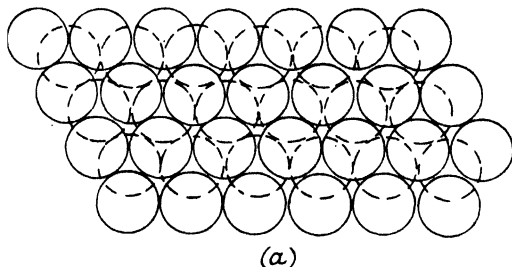


FIG. 11 (a).—Close-Packed Hexagonal Lattice, Atom Space Model.

well-known types of space lattice and they can be produced by packing spheres much more closely together. These types of lattice are known as the close-packed hexagonal lattice and the face-centred cubic lattice respectively, and we shall deal with them in that order. If the first layer of closely packed spheres is arranged as shown in Fig. 11 (a) by means of the full circles, then the second layer can be formed by resting spheres in hollows so that they are in contact with three spheres of the first layer. In doing this it will be noticed that it is *impossible*

to rest the dashed circles, representing the second layer spheres, so that all of the hollows of the first layer are covered. The third layer may be formed in two ways, one of which involves repeating the first layer so that the third layer spheres are placed directly over their counterparts in the first layer. The

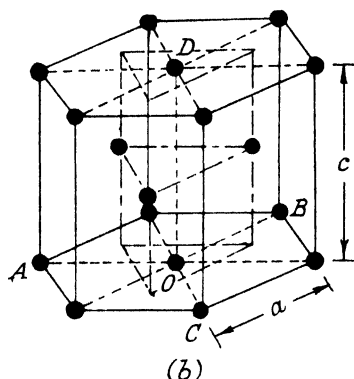


FIG. 11 (b).—Close-Packed Hexagonal Lattice Unit.

lattice unit of this structure—the close-packed hexagonal lattice—is shown in Fig. 11 (b), and this is repeated throughout the space of a crystal grain of metals like magnesium, zinc, cadmium and titanium, which are characterised by this type of lattice. Each of the corner atoms is shared by six lattice units, so that of the twelve

corner atoms only $\frac{12}{6} = 2$ “ be-

long ” to the unit ; each of the two face-centred atoms is

shared by two units, so that of these only $\frac{2}{2} = 1$ “ belongs ” to

the unit ; the three internal atoms are totally enclosed by the unit, which therefore holds $2 + 1 + 3$, i.e. 6 atoms. The density formula in this case is therefore :

$$\text{Density} = \frac{\text{Weight of hydrogen atom} \times \text{Atomic weight of metal} \times 6}{\text{Volume of hexagonal lattice unit}}.$$

It may be shown that the closest packing of the spheres occurs when the axial ratio—i.e. $\frac{c}{a}$ —is equal to $\sqrt{\frac{8}{3}} = 1.633$.

The Face-Centred Cubic Lattice. The other method of close packing of spheres, based on the alternative arrangement of the third layer, is shown in Fig. 12 (a). The second layer of spheres, shown by dashed circles, are placed as before, but the third

layer, shown by dotted circles, is so arranged that the spheres fall directly over those hollows in the first layer which were not directly covered by the spheres of the second layer. The fourth layer, which is not shown in the diagram, is then produced by spheres which come directly over their counterparts in the first layer, and the arrangement repeats itself with successive layers. The unit of the lattice so constructed, known as the face-centred cubic or the cubic close-packed lattice, is shown in Fig. 12 (b). The connection between Fig. 12 (a) and (b) may perhaps best be visualised by imagining the lattice

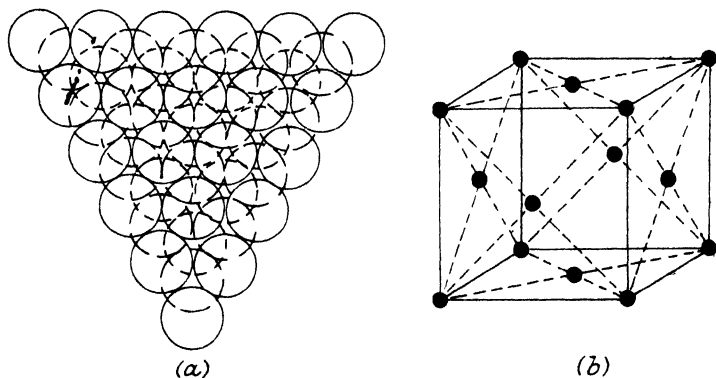


FIG. 12 (a).—Face-Centred Cubic Lattice, Atom Space Model. (b). Face-Centred Cubic Lattice Unit.

unit placed so that one of the cube diagonals is perpendicular to the plane of the paper. Under such conditions the top corner atom would be in the fourth layer, and if the horizontal layers are gradually removed, three of these will have to be taken away before the opposite corner atom is exposed in the bottom layer. It may easily be shown that the number of atoms per face-centred cubic lattice unit is four and the density equation may be modified accordingly. Metals with face-centred cubic lattices include γ -iron, nickel, copper, silver, gold, platinum, lead and aluminium. The difference between the

X-ray diffraction patterns of face-centred cubic and body-centred cubic metals is shown in Fig. 13. It might be mentioned at this stage that X-ray examination has shown why it is that there is a definite contraction in volume and increase in density when α -iron changes to γ -iron at the A_{c_3} point (900°C.), at which there is a change of arrangement of the iron atoms from that of the rather loosely packed body-centred cubic lattice of the α -iron to that of the cubic close-packed lattice of the γ -iron. It should also be noted that the face-centred cubic



FIG. 13 (a).—X-Ray Diffraction Photograph. Annealed Specimen of Aluminium, Typical Face-Centred Cubic Metal.



FIG. 13 (b).—X-Ray Diffraction Photograph. Annealed Specimen of Tungsten, Typical Body-Centred Cubic Metal. (Note Change of Pattern with Change of Lattice Form.)

metals are almost without exception malleable and ductile, but the relationship between mechanical properties and crystal structure must be left for more detailed discussion later.

Other Space Lattices in Metals. The three lattices previously described are by far the most common in metals, but we must briefly refer to three others which are occasionally encountered. These are : (a) The *rhombohedral hexagonal lattice*, in which the atoms are arranged in repeated double layers so that each atom has three close neighbours in the one layer and three at a greater distance in the other layer. Such a lattice is found in antimony and bismuth, in which the grouping of the atoms into

threes is accounted for by the need for covalent linkage, which occurs by the sharing by one atom of electrons provided by three others. These elements therefore form crystals which are built up of atoms joined by covalent rather than purely metallic linkages. (b) The *tetragonal lattice*, the unit of which is an elongated cube, which may be body-centred, as in β -tin, or face-centred, as in indium. (c) The *tetrahedral cubic lattice*, which is of the diamond type and in which each atom has four covalently held neighbours. This type of lattice is found in germanium and α -tin. The crystal structures of all the metals, except manganese, the lattice of which may be particularly complex, can be included in one or another of the above types.

CHAPTER V

ATOM PLANES, ATOM DIRECTIONS AND INTER-ATOMIC DISTANCES IN METAL CRYSTALS

Crystallographic Planes. We have seen that the atoms or ions of metallic crystals are arranged in a perfectly orderly way throughout the space of each individual grain and that the number of such arrangements or lattices found in these crystals is strictly limited. The common lattices are described as body-centred cubic, close-packed hexagonal and face-centred cubic, while the less common forms are known as rhombohedral hexagonal, tetragonal and tetrahedral cubic. It is, from many points of view, convenient when dealing with the behaviour of the grains themselves to consider the complete lattice as being built up of planes of atoms called crystallographic planes. Each

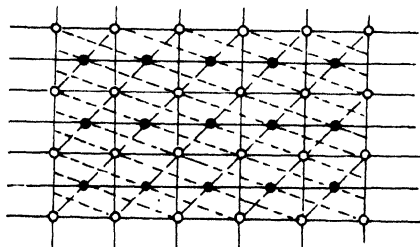


FIG. 14.—Three Sets of Planes in a Body-Centred Cubic Lattice.

particular lattice is characterised by a number of sets of crystallographic planes which may be visualised as passing through the centres of the atoms in such a way that all the planes of one set are parallel to one another but that they vary in orientation from one set to another. A set of crystallographic planes may thus be defined as a series of planes which pass through the centres of the atoms and are so arranged in space that every plane passes through the centres of some of the atoms and every atom is contained in at least one of the planes in the series concerned.

Before passing on to discuss the actual crystallographic planes found in the characteristic lattices it will be as well to consider the way in which the packing of the atoms in any one set of planes is related to the distance between the planes of that particular set. We can do this by referring to Fig. 14, which represents the plan of a body-centred cubic lattice, the white circles corresponding to the centres of lattice unit corner atoms and the dark circles to the atoms at the centres of the unit cubes. The three sets of parallel lines passing through all of the atom circles represent the intersection with the plane of the paper of the corresponding vertical sets of crystallographic planes. It is seen that the atoms are most closely packed in the set of planes most widely separated, while the atoms are well apart in the set of planes which happen to be closest together. This may be deduced directly from the statement that the number of atoms per unit volume is constant.

Crystallographic Plane Notation. We may now proceed to deal with the individual sets of atom planes. In order to describe and define the position in space of these sets of planes we shall need to use a special form of crystallographic notation. This notation is used to define a plane, or set of planes, in terms of the number of parts into which the set of planes divides the edges of the unit of the lattice under consideration. Thus, Fig. 15 represents the unit of the fundamental *cubic* lattice; it might be emphasised that such a simple unit is *not* found in actual metal crystals. The cube of side a is intersected by a number of planes, portions of which are shown in the diagram, in such a way that the side OA is divided into three parts, the side OB into two parts and the side OC into one part; the actual intercepts are of length $\frac{a}{3}$, $\frac{b}{2}$ and $\frac{c}{1}$ respectively. The set of planes shown in Fig. 15 is defined as consisting of the three, two, one planes and is denoted as follows: (321); in other words, the planes shown are the (321) planes.

Defined Sets of Planes. There are, of course, quite a number of sets of crystallographic planes to be found in a simple cubic lattice, and, in connection with their definition, reference to Fig. 16 will enable the following points to be made :

(i) The set of planes parallel to and including the planes $OBFC$ and $ADGE$ are defined as (100) planes.

(ii) The sets of planes including $OAEC$ and $BDGF$, and $OADB$ and $CEGF$ are similarly spaced and similarly related

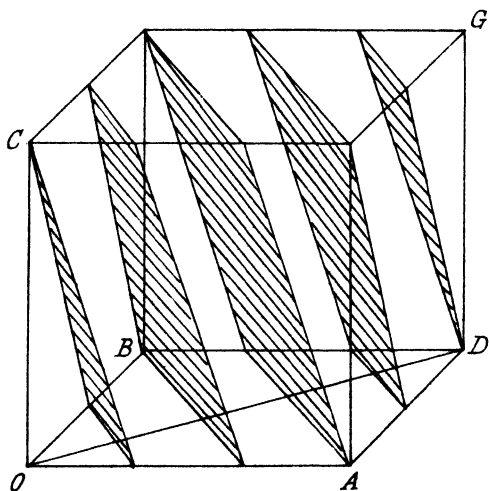


FIG. 15.—Showing (a) a (321) Set of Planes ; (b) that the (111) Direction lies in the (321) Planes (*vide* p. 55).

to the lattice as a whole, and are therefore included with the other (100) planes, although these sets of planes would be respectively defined as (010) and (001) planes.

(iii) There are in a cubic lattice three sets of (100) planes.

(iv) The planes including $ABFE$ and also passing through OC and DG are the (110) planes, and there are six sets of these, parallel respectively to $ABFE$, $ODGC$, $ACFD$, $OEGB$, $GAOF$ and $EDBC$.

(v) The set of planes parallel to ABC are denoted as (111) planes. There are four sets of (111) planes, parallel respectively to ABC, ABG, ODE and ODF.

(vi) It has been found possible to calculate the number of sets of planes with a given index as follows :

- (a) If all the numbers are different and not one is nought, e.g. (321), then the number of sets of such planes is 24.

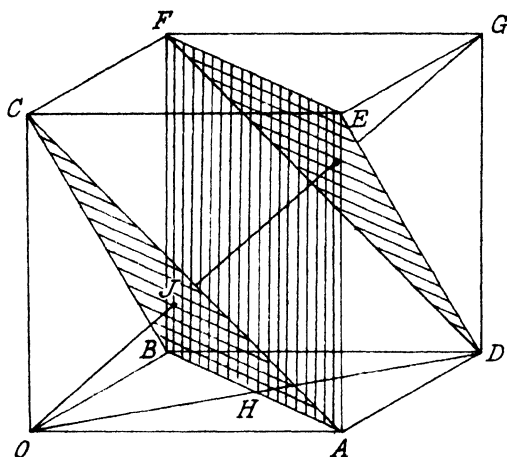


FIG. 16.—Showing (a) Notations of Various Sets of Planes ; (b) Distances between Sets of Planes.

- (b) If two of the numbers are the same and not one is nought, e.g. (112), then the number of sets of such planes is $\frac{24}{2} = 12$.

- (c) If the three numbers are the same, e.g. (111), then the number of sets of such planes is $\frac{24}{6} = 4$.

- (d) If two numbers are the same and one is nought, e.g. (110), then the number of such sets of planes is $\frac{24}{4} = 6$.

- (e) If there are two noughts as, e.g. in (100), then the number of such sets of planes is $\frac{24}{8} = 3$.

Distance Between Planes of a Given Set. Having shown how it is possible by means of a simple notation to define the positions in space of the different sets of crystallographic planes, we must now deal with the problem of determining the distances between successive planes of any one particular set. It is, for a start, fairly obvious at once that in a cubic lattice the distance between successive (100) planes is equal to the lattice parameter a . The corresponding distances for other planes may be deduced by referring to Fig. 16. Thus, the distance between the (110) planes is equal to $OH = OD/2 = \sqrt{2}.a/2 = a/\sqrt{2}$. Similarly, the distance between the (111) planes is equal to $OJ = OG/3 = \sqrt{3}.a/3 = a/\sqrt{3}$. In the general case of the planes with index (hkl) it can be shown that the interplanar distance d is given by $d = a/\sqrt{h^2 + k^2 + l^2}$. This general equation shows that the most widely spaced planes are those with the simplest indices—(100), (110) and (111), the distances decreasing in the order given.

Crystallographic Planes in Face-Centred Cubic Metal Lattices.

We must now consider those sets of crystallographic planes in actual metal lattices which do in fact pass through all the atom centres. In a face-centred cubic lattice (Fig. 17) all of the atoms are included in the (111) set of planes, among which are the planes ACB and EFD, but the face-centred atoms are not included in the (100) planes. In order that these atoms might be included we must consider the set involving the planes OBFC, HJKL and ADGE. This set of planes contains all of the atoms and has the index (200). Similarly, in order to include the face-centred atoms in the set parallel to the plane AEFB, we must specify planes with index (220) rather than those with index (110). Thus the planes with simplest indices in the face-centred cubic lattice are those with the indices (111), (200) and (220).

Crystallographic Planes in Body-Centred Cubic Metal Lattices.

The same method of approach may be adopted in dealing with the body-centred cubic lattice, the unit of which is shown in Fig. 18. All of the atoms in this lattice lie in the (110) and (200) sets of planes, which include respectively the planes AEFB and HJKL. In order to include the body-centred atom N in planes of the type (111) the set must be written (222). The simplest index planes for a body-centred cubic lattice are thus those with the indices (110), (200) and (222).

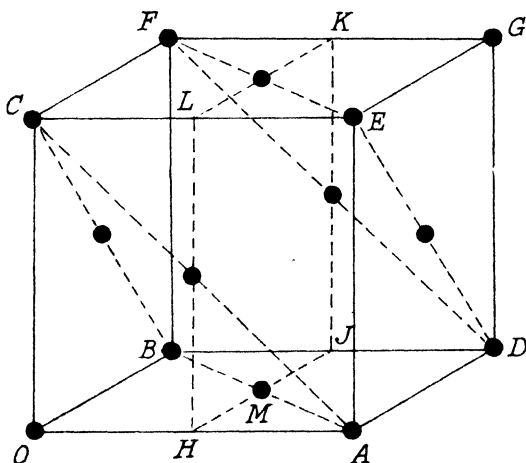


FIG. 17.—Sets of Planes in a Face-Centred Cubic Lattice.

Face-Centred Cubic Lattices—The General Case. It is possible to determine beforehand whether a given set of planes will pass through the centres of all the atoms of a face-centred or body-centred cubic lattice. The method used to do this is based on the following line of reasoning. Dealing first with the face-centred cubic lattice, it may be pointed out that a set of planes with h intercepts on OA and k intercepts on OB will have $h+k$ intercepts on the diagonal OD (see, e.g. Fig. 15). The face-centred atom M will lie in one of these planes only if

$h+k$ is even. It may similarly be shown, if the set makes l intercepts on OC, that the other face-centred atoms will be in the sets of planes only if $k+l$ and $l+h$ are even. If $h+k$, $k+l$ and $l+h$ are all even, then h , k and l must be *all even* or *all odd*. The following are therefore sets of planes passing through *all* (viz. corner and face-centred) atoms in a face-centred cubic lattice: (111), (200), (220) and (311).

Body-Centred Cubic Lattices—The General Case. Passing to the body-centred cubic lattice (Fig. 18), if, as before, the number

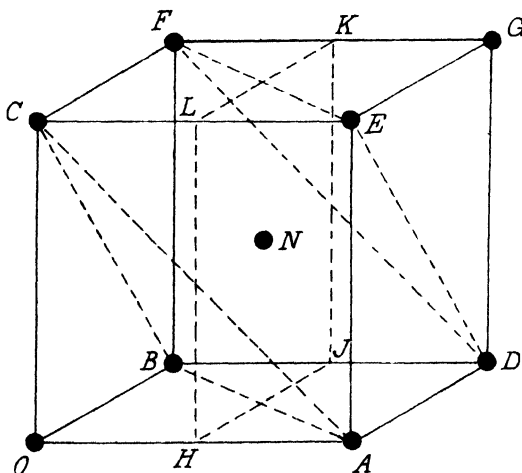


FIG. 18.—Sets of Planes in a Body-Centred Cubic Lattice.

of intercepts of a given set of planes on the axes OA, OB and OC are respectively h , k and l , then the cube diagonal OG is divided into $h+k+l$ parts (see, once again, Fig. 15). In order that the body-centred atom N might fall on one of the planes, $h+k+l$ must be *even*; and this is the condition to be satisfied before any set of planes can pass through all the atoms of a body-centred cubic lattice; typical sets of such planes are given by the indices (110), (200), (211), (222) and (310).

CRYSTALLOGRAPHIC DIRECTIONS

We have seen how sets of crystallographic planes may be defined by means of suitable indices of the type (hkl) , that these planes are separated by a distance given by $d = a/\sqrt{h^2 + k^2 + l^2}$, that in face-centred cubic lattices the sets of planes are defined by indices in which h , k and l are either all even or all odd, thus: (111) , (200) , (220) , etc.; and that in body-centred cubic lattices the similarly defined sets of planes are found when the sum of $h + k + l$ is an even number, e.g. (110) , (200) , (211) , etc. In order to complete the discussion of crystal orientation we must now deal with the method of describing a *crystallographic direction*, i.e. a line which passes through the centres of atoms arranged in a crystallographic plane.

Direction Notation.

The notation employed for this purpose is similar in appearance to that previously described, only the indices representing crystallographic directions are enclosed in square brackets to differentiate them from the corresponding indices for crystallographic planes. Whereas a plane (or set of planes) is represented by an index of the type (hkl) a direction is stated in the form $[pqr]$. We may, once again, take a simple cubic lattice for purposes of illustration (Fig. 19), with the help of which it may be stated that a crystallographic direction is defined as a line joining the origin O to the point P , the co-ordinates of which are: OA in the direction OA , AD

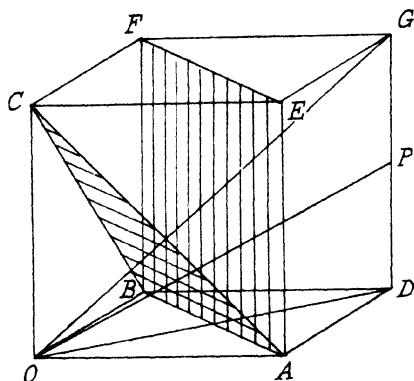


FIG. 19.—Showing (a) Crystallographic Directions in a Cubic Lattice; (b) Relation of Direction to Plane of same Index.

(equal to OB) in direction OB, and DP (equal to one-half OC) in the direction OC—i.e. $1 \times a$, $1 \times a$, $\frac{1}{2} \times a$. Thus the direction OP is written $[11\frac{1}{2}]$, or, in order to remove fractional indices, $[221]$. The more common crystallographic directions OA, OD and OG are thus expressed as the $[100]$, $[110]$ and $[111]$ directions respectively. It might be mentioned that the directions OB and OC, which are correctly written respectively as $[010]$ and $[001]$, are similarly related and are usually included in the $[100]$ class. In the same way the correspondingly related directions are included in the $[110]$ and $[111]$ classes.

Relation of Directions to Planes of Same Index. It is useful to note that there are the same number of directions of a given index as there are sets of planes with the same index. Thus, there are four $[111]$ directions, i.e. four cube diagonals, in just the same way as there are four sets of (111) planes; similarly, there are six $[110]$ directions as there are six (110) planes and three $[100]$ directions corresponding to the three (100) sets of planes.

Another important relationship is that the direction of a given index is perpendicular to the set of planes of the same index. The truth of this statement is easily confirmed by referring once again to Fig. 19; the line OG—a $[111]$ direction—is perpendicular to the (111) plane ABC; the line OD—a $[110]$ direction—is perpendicular to the (110) plane ABFE; finally, the line OA—a $[100]$ direction—is, in turn, perpendicular to the (100) plane ADGE.

Planes, Directions and Plastic Deformation. When dealing with the modern interpretation of the mechanism of plastic deformation of metals and alloys and with the associated problems of hardness and strength—resistance to plastic deformation—we find it essential to be familiar with the more important crystallographic planes and crystallographic directions. We shall, therefore, with this in mind, devote our attention now to a brief discussion of the planes and directions of the atoms in the three main types of metal crystal lattices

in the order : face-centred cubic, body-centred cubic and close-packed hexagonal respectively. It will be found most convenient to deal with these by examining atom space models, built up of spheres as previously described (Figs. 12, 10 and 11), and now shown in Figs. 20, 21, 22.

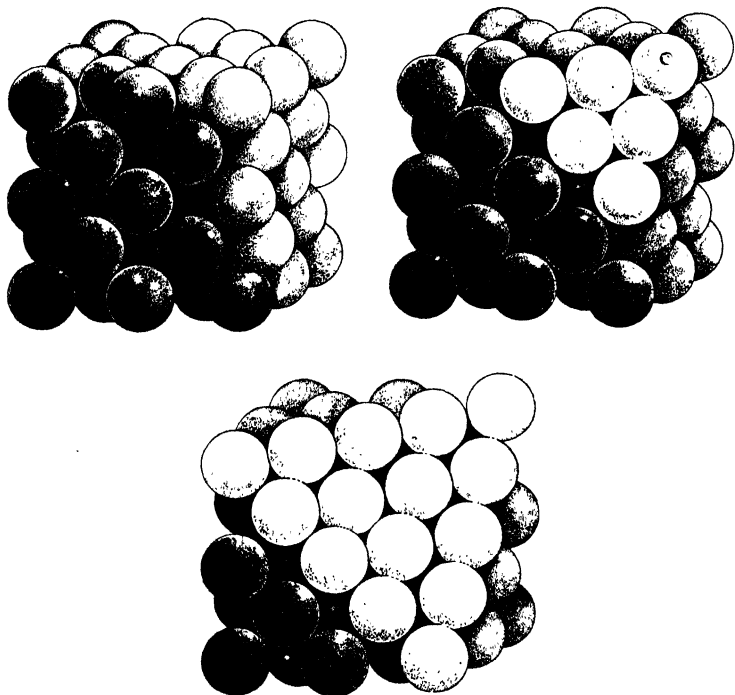


FIG. 20.—Models Illustrating Face-Centred Cubic Atomic Arrangement.

[By permission of Dr. W. Hume-Rothery and The Institute of Metals]

If the corner atom spheres and the layers immediately under them are removed from a cube model representing the placing together of eight face-centred cubic lattice units (Figs. 12 and 20) there are exposed four sets of (111) planes in which the atoms are as closely packed as possible, each atom having six close neighbours in the plane concerned and the neighbouring

atoms forming the hexagon around the original atom in the way which characterises the close packing of spheres. The close-packed (111) planes are the ones along which gliding takes place when the grains of face-centred cubic metals and alloys are deformed. It is readily seen from the model that there are in each of the (111) planes three directions—the [110] directions—in which the atom spheres are so closely packed that they are in actual contact. The gliding which occurs during the deformation along the (111) planes does in fact take place along the [110] directions. The position may be summarised

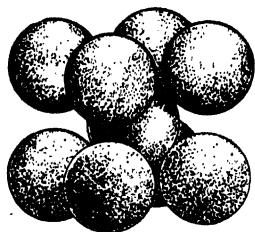


FIG. 21.—Model Illustrating Body-Centred Cubic Atomic Arrangement.

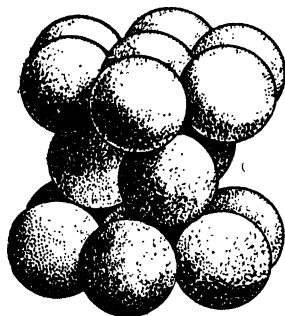


FIG. 22.—Model Illustrating Close-Packed Hexagonal Atomic Arrangement.

[By permission of Dr. W. Hume-Rothery and The Institute of Metals]

as follows: The marked malleability and ductility associated with face-centred cubic metals is due to the presence of the four sets of closely packed (111) planes in which there are six sets of closely packed [110] directions; the planes themselves provide the means of gliding and the directions indicate the alternative linear routes available for the motion; the *minimum* movement involved during gliding is naturally the distance from the centre of one atom to the next, and this explains the readiness with which it occurs in the planes and along the directions of close atomic packing so readily available in the face-centred cubic lattice.

The model of the body-centred cubic lattice unit (Figs. 10 and 21) shows the complete absence of *closely* packed planes of atoms—the lattice being, indeed, characterised by the presence of open spaces—but there is a set of *directions* in which the atoms are in contact with each other. The absence of close-packed atom planes makes the plastic deformation of metals and alloys with body-centred cubic lattices take place, in general, much less readily than it occurs with the corresponding face-centred materials. When deformation does take place, it is, however, usually found to do so in the $[111]$ directions, i.e. along the lines of the close-packed atoms.

The plastic deformation properties of α -iron or ferrite are, for a body-centred cubic metal, in many respects exceptional; it would therefore seem desirable to discuss this briefly. In α -iron, as in other body-centred cubic metals, the slip direction is the one of closest atomic packing, i.e. the $[111]$ direction. There are, of course, no planes of closely packed atoms; in other words, the distance between the planes is never the maximum associated with atom close packing (p. 45). There are, however, a number of planes of decreasing but relatively distant spacing, and these are respectively the planes given by the indices (110), (200), (211), (222), (310) and (321) (*vide* p. 50). These are not all available for gliding, since this can only occur in $[111]$ directions. Gliding can therefore only occur in those of the relatively distant planes which contain a $[111]$ direction, viz. the (110), (211) and (321) planes. It is of interest in this particular connection to refer to Fig. 15 (p. 46), which shows that the $[111]$ direction in the form of the cube diagonal from A to the opposite corner does lie in one of the (321) planes; the reader might verify for himself that the $[111]$ direction is also included in the (211) and (110) planes. The planes along which gliding may therefore occur in body-centred cubic metals in the $[111]$ directions are the (110), (211) and (321) planes, and of these there are six, twelve and twenty-four sets respectively (*vide* p. 47). It is important at this stage to

remember that plastic deformation involves, in addition to gliding along planes of relatively close atomic packing, actual rotation of the gliding planes so as to bring them gradually into the plane of maximum resolved shear. In ferrite there are so many sets of otherwise practically equivalent glide planes available that the amounts of angular rotation needed in the individual grains before slip can occur, first on one set of planes and then on another, are comparatively small. There appears to be found here a possible explanation of the exceptional yield-point of multicrystalline α -iron; it is conceivable that each individual grain can yield on so many planes after comparatively slight increments of rotation that the yield of the mass of grains is quite pronounced although the necessary increment of stress required to produce it is small.* It should be mentioned that other body-centred cubic metals do not appear able to deform with anything like the same facility; in tungsten, for example, the gliding seems practically confined to the (110) planes.

The close-packed hexagonal space model (Figs. 11 and 22) clearly shows that the planes of closest packing of the atom spheres are the first, third, fifth, etc., layers. In this type of lattice the crystallographic axes (Fig. 11b) are OA, OB, OC and OD, so that the close-packed planes along which gliding occurs are the (0001) planes.† The close-packed lines along which slip takes place are in the directions OA, OB and OC, which may be expressed in crystallographic notation as the [1000], [0100] and [0010] directions respectively.

* Those interested in the fundamental problem of the yield-point in ferrite are advised to consult "The Yield Point in Steel," by C. A. Edwards, D. L. Phillips and Y. H. Liu (*Journal of the Iron and Steel Institute*, Vol. I, 1943).

† Note the need for *four* numbers in the index for this set of planes in the close-packed hexagonal lattice. The intercepts (p. 45) are 0 on axis OA, 0 on axis OB, 0 on axis OC and 1 on axis OD.

INTERATOMIC DISTANCES AND ATOMIC DIAMETERS

We have already made the general statement that when any two metals are used to form an alloy the actual structure of the alloy depends on whether, for the metals concerned, the tendency to produce a solid solution is greater than the opposing tendency to form an intermetallic compound. Since the formation of solid solutions is mainly governed by the relative sizes of the two atoms, while compound formation involves relationships between the atoms and their extra-nuclear electrons, it is probably more convenient to discuss first the sizes of metal atoms, usually expressed in terms of atom diameters. We have recently shown that in all types of pure metal crystals there are certain directions of atom close packing, and if, as is convenient, we continue to regard atoms as spheres, it is readily seen that the shortest interatomic distances are of the same magnitude as the respective atomic diameters. We shall therefore proceed to discuss the closest distance of approach of atoms in the typical metallic lattices.

Minimum Interatomic Distance in Body-Centred Cubic Metals. In the body-centred cubic lattice (Figs. 10 and 21) the direction of closest atomic packing is the $[111]$ direction—i.e. the cube diagonal. It may be shown that if the cube side or lattice parameter is a , then the face diagonal is equal to $\sqrt{a^2 + a^2} = \sqrt{2} \cdot a$ and the cube diagonal is equal to $\sqrt{2a^2 + a^2} = \sqrt{3} \cdot a$. There is an atom at each end of the cube diagonal and also one at its centre, so that the closest distance from atom centre to atom centre is $\sqrt{3} \cdot a/2$. It will be remembered that X-ray diffraction furnishes a means of directly measuring the lattice parameter a ; by using such data it is therefore possible to calculate exactly the closest distance of interatomic approach, *which amounts to the same thing as the actual diameter of the atom sphere*. Some typical results of such calculations applied to body-centred cubic metals are given in Table V.

TABLE V.—ATOMIC DIAMETERS OF SOME BODY-CENTRED CUBIC METALS

<i>Metal</i>	<i>Closest Interatomic Distance or Atomic Diameter (\AA)</i>
Sodium	3.71
Potassium	4.62
α -Iron	2.48
Molybdenum	2.72
Tungsten	2.74

It should be mentioned here that in a body-centred cubic lattice each atom has eight neighbours, all at the same close interatomic distance from it. Metals with a body-centred cubic lattice are therefore said to possess a *co-ordination number* of eight.

Minimum Interatomic Distances in Face-Centred Cubic Metals. An examination of the unit of a face-centred cubic lattice (Figs. 12 and 20) shows that in this case the atoms are packed most closely in the $[110]$ directions, i.e. along the cube face diagonals. The lengths of these diagonals are given by $\sqrt{2} \cdot a$, so that here the distance of closest approach of the atoms is $\sqrt{2} \cdot a/2$. The evaluation of this quotient gives the magnitude of the atomic diameter in the case of metals with face-centred cubic lattices, some typical figures being given in Table VI.

TABLE VI.—ATOMIC DIAMETERS OF SOME FACE-CENTRED CUBIC METALS

<i>Metal</i>	<i>Closest Interatomic Distance or Atomic Diameter (\AA)</i>
Aluminium	2.86
γ -Iron	2.52
Copper	2.55
Silver	2.88
Gold	2.88
Lead	3.49

Since in lattices of the face-centred cubic type each atom has twelve close neighbours—six in the same sphere layer, three below and three above—metals with face-centred cubic lattices are said to have a *co-ordination number* of twelve.

Interatomic Distances in Close-Packed Hexagonal Metals. The close-packed hexagonal lattice is characterised by a unit consisting of a hexagonal figure, the side of the hexagon being a and its height being c (Figs. 11 and 22). An atom at O, for

example, has six close-packed neighbours in the same layer, all at a distance a from O, and has three neighbours in the layer above and three in the layer below. The latter six atoms are usually at a distance from O which is greater than a , although when the axial ratio c/a is equal to 1.633 all twelve neighbouring atoms are at the same distance a from O. Thus, in metals with the close-packed hexagonal lattice each atom has twelve close neighbours (*co-ordination number* 12) which may all be equidistant from the original atom or which are divided into two groups, six at one distance and six others at a slightly greater distance away. In the latter case it is usually found that the two distances are of approximately the same order of magnitude, so that in close-packed hexagonal lattice metals the atomic diameters are roughly the average of the two interatomic distances. Typical data for metals with close-packed hexagonal lattices are summarised in Table VII.

TABLE VII.—INTERATOMIC DISTANCES AND ATOMIC DIAMETERS FOR SOME CLOSE-PACKED HEXAGONAL METALS

Metal	Axial Ratio c/a	Interatomic Distances (Å)		Atomic Diameter (Å)
Beryllium . .	1.57	2.22	2.28	2.25
Magnesium . .	1.62	3.19	3.20	3.20
Titanium . .	1.60	2.91	2.95	2.93
Zinc . .	1.86	2.66	2.91	2.75
Cadmium . .	1.89	2.97	3.29	3.04

It might be mentioned that the co-ordination numbers which characterise metals are eight (body-centred cubic), twelve (face-centred cubic) or six and six (close-packed hexagonal). It is only in crystals of the tetrahedral cubic or diamond type that individual atoms have only four close neighbours. Elements with lattices of this type are therefore characterised by a co-ordination number as low as four.

Atomic Diameter and Co-ordination Number of Lattice. We now come to the question as to whether the atomic diameter—viz. the diameter of the hypothetical atom sphere—is, like the

60 *Atomic Diameter and Co-ordination Number of Lattice*

atomic number, invariable and constant. There is much evidence to show that such is not the case and that the diameter of the atom is largely governed by the co-ordination number of the crystal lattice with which the atom happens to be associated. It must not be thought that metal atoms are incapable of taking up positions in lattices other than those characteristic of the pure metal itself. Thus, for example, atoms of close-packed hexagonal zinc can take substitutional positions in the face-centred cubic lattice of copper, forming α -brasses, and again, atoms of aluminium (face-centred cubic) can similarly be present in the body-centred cubic lattice of α -iron. It is under such circumstances—e.g. in different lattices—that the atomic diameters appear to change, being characterised by a magnitude which is governed by the co-ordination number of the particular lattice in which the atom happens to be ; in other words, atoms appear to have different sizes when they are in different lattices. When we consider the way in which the atom diameter varies from one lattice to another it may be taken that the closer the atomic packing the larger does the atom appear. Thus, atoms of a face-centred cubic or close-packed hexagonal metal (co-ordination number 12) apparently become smaller when they assume (in solid solution or otherwise) a body-centred cubic lattice with co-ordination number 8. It has, in fact, been shown that there is a 3 per cent. contraction in passing from co-ordination number 12 to co-ordination number 8, and that a knowledge of the atomic diameter under one set of lattice conditions enables its calculation under another. Much of the pioneer work in the calculation of atomic diameters by these and other methods has been carried out by Goldschmidt, and the resulting figures are sometimes quoted for the respective metals as representing their Goldschmidt atomic diameters. The figures thus obtained are of the same order of magnitude as the previously described interatomic distances. A summary of the crystallographic data for most of the important metals is given in Table VIII.

TABLE VIII.—SUMMARY OF METAL CRYSTALLOGRAPHIC DATA

Metal	Sym- bol	At- omic Num- ber	Atomic Weight	Normal Val- ency Elec- trons	Lattice Type(s)	Atoms per Lat- tice Unit	Para- meter <i>a</i> <i>c</i>	Inter- atomic Distances Å
Lithium	Li	3	6.94	1	b.c.c.	2	3.50	3.03
Beryllium	Be	4	9.02	2	c.p.h.	6	2.28 3.58	2.22 2.28
Sodium	Na	11	22.997	1	b.c.c.	2	4.28	3.71
Magne- sium	Mg	12	24.32	2	c.p.h.	6	3.20 5.20	3.19 3.20
Alu- minium	Al	13	26.97	2, 1	f.c.c.	4	4.04	2.86
Potas- sium	K	19	39.096	1	b.c.c.	2	5.33	4.62
Calcium	Ca	20	40.08	2	f.c.c.	4	5.56	3.93
Titanium	Ti	22	47.90	2	c.p.h.	6	2.95 4.73	2.92 2.95
Vanadium	V	23	50.95	2	b.c.c.	2	3.03	2.63
Chro- mium	Cr	24	52.01	1	α b.c.c.	2	2.88	2.49
					β c.p.h.	6	2.72 4.42	2.71 2.72
Man- ganese	Mn	25	54.93	2	α cubic	58	8.89	
					β complex	20	6.29	
					γ tetrag.	4	3.77 3.53	2.58 2.67
Iron	Fe	26	55.85	2	α b.c.c.	2	2.86	2.48
					γ f.c.c.	4	3.56	2.52
Cobalt	Co	27	58.94	2	α c.p.h.	6	2.51 4.07	2.50 2.51
					β f.c.c.	4	3.54	2.51
Nickel	Ni	28	58.69	2	α c.p.h.	6	2.49 4.08	2.49 2.49
					β f.c.c.	4	3.52	2.49
Copper	Cu	29	63.57	1	f.c.c.	4	3.61	2.55
Zinc	Zn	30	65.38	2	c.p.h.	6	2.66 4.94	2.66 2.91
Molybde- num	Mo	42	95.95	1	b.c.c.	2	3.14	2.72
Silver	Ag	47	107.88	1	f.c.c.	4	4.08	2.88
Cadmium	Cd	48	112.41	2	c.p.h.	6	2.97 5.61	2.97 3.29
Tin	Sn	50	118.7	2, 2	α t.c.	8	6.46	2.80
					β b.c.t.	2	5.82 3.18	3.02 3.18
Antimony	Sb	51	121.76	2, 2, 1	rh.	2	4.50	2.90 3.36
Tungsten	W	74	183.92	2	α b.c.c.	2	3.16	2.74
Platinum	Pt	78	195.23	2	f.c.c.	4	3.92	2.77
Gold	Au	79	197.2	1	f.c.c.	4	4.07	2.88
Mercury	Hg	80	200.61	2	rh.	1		3.00
Lead	Pb	82	207.21	2, 2	f.c.c.	4	4.94	3.49
Bismuth	Bi	83	209.00	2, 2, 1	rh.	2	4.74	3.10 3.47

b.c.c. body-centred cubic

f.c.c. face-centred cubic

c.p.h. close-packed hexagonal

t.c. tetrahedral cubic

b.c.t. body-centred tetragonal

rh. rhombohedral

CHAPTER VI

SOLID SOLUTION AND SOLID SOLUBILITY

Solid Solutions. An examination of the many published equilibrium diagrams for binary alloy systems shows that generally the addition of one metal to another does not immediately result in the production of a new phase. The normal tendency is, in fact, for a solid solution to form, and it appears at first that the extent of the solid solubility depends on certain characteristics of the metals concerned, but seems to vary in a haphazard way when we pass from one alloy system to another. During the last ten years much research work has been carried out on the problems of solid solution and solid solubility, and we are now in a position to discuss the results in some detail. It has been shown that formation (or otherwise) of solid solution and extent of solid solubility can, in most cases, be perfectly satisfactorily explained.

Types of Solid Solution. There are two types of metallic solid solution—substitutional solid solution and interstitial solid solution—and, so far, research has been mainly confined to the former type. A substitutional solid solution is characterised by the fact that it retains the lattice of the solvent metal and that atoms of the solute metal are able, usually to a limited extent, to replace those of the solvent without unduly distorting the parent lattice of the solvent. This naturally leads to the idea that one, at least, of the factors influencing solid solubility of this type is the relative sizes of the atoms of the two metals under consideration, although, as we shall see later, size-factor alone is incapable of explaining solid solubility variations. It might be mentioned here that it is usual to find that in substitutional solid solutions there is a random arrangement of atoms of the solute metal in the lattice of the solvent even at

ordinary temperatures. However, although in some cases the solute atoms are disordered at high temperatures, under suitable conditions, e.g. very slow cooling or low-temperature annealing, they can rearrange themselves in a perfectly orderly way in the regular lattice of the solvent, thus producing what is known as a *superlattice* (*vide* p. 77). The formation of a substitutional solid solution, owing to differences in the sizes of the solvent and the solute atoms, normally involves a gradual expansion or contraction of the lattice parameter. In fact, the lattice parameter of a solid solution varies practically linearly with increasing *atomic* percentage of solute metal; the deviations from this rule which occur usually involve a contraction as compared with a definite linear relationship. When superlattices are formed there are quite abnormal changes of lattice parameter with changes of atomic composition.

The Size-Factor Effect. The importance of "size-factor" in determining whether a solid solution may form between any two metals was first demonstrated in 1934 by Hume-Rothery and his co-workers. They studied solid solutions of various metals in both copper and silver and were able to state the following general principle: If the atomic diameters of the solvent and solute differ by more than about 14 per cent. of that of the solvent, the size-factor is unfavourable and the solid solution is very restricted, whilst when the atomic diameters are within this limit the size-factor is favourable, and considerable solid solutions *may* be formed. These workers decided to use the interatomic distances, which are characteristic of the metals concerned, as indicators of the respective atomic diameters, although they found that the figures required minor corrections in certain cases, as, for example, in the case of metals like aluminium, which appeared to be incompletely ionised in crystals of the pure metal.

The mode of application of the Hume-Rothery Size-Factor Rule may be facilitated by reference to Fig. 23, in which interatomic distances (atomic diameters), in Ångstrom units, are

shown for the solvent metals copper and silver and for the solute metals zinc, magnesium, cadmium and beryllium; the horizontal broken lines indicate the limits of the 14 per cent. favourable size-factor range for copper, while the similar dotted lines outline the limits of the corresponding range for the silver atom. It will first be noted that magnesium is outside the favourable range for copper, and beryllium is similarly

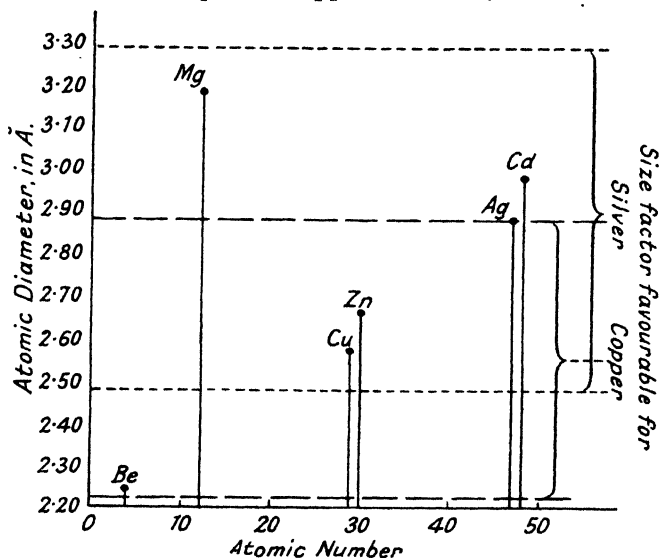


FIG. 23.—Effect of Size Factor on Solid Solubilities in Copper and Silver.

outside the favourable range for silver, so that we should expect to find that the solid solubility of magnesium in copper and of beryllium in silver is in each case low. The published figures substantiate this deduction and are given respectively, as atomic percentages at maximum solid solubility, as 6.5 per cent. Mg in Cu and 3.5 per cent. Be in Ag.

On the other hand, beryllium is within the favourable range for copper, and magnesium is similarly situated with regard to the possibility of extended solid solution in silver; once again

the most reliable published figures are in agreement, and may be expressed, on the same basis, as 16.6 per cent. Be in Cu and *ca.* 30 per cent. Mg in Ag.

Dealing now with the solute elements zinc and cadmium it will be observed that while zinc is in the favourable zones for both copper and silver, cadmium is within the favourable zone for silver but outside the one for copper. Thus we expect to find extended solid solubility for zinc in both copper and silver, and extended solid solubility of cadmium in silver but restricted solid solubility of cadmium in copper. Again our expectations prove correct, for the appropriate published figures are 38.4 per cent. Zn in Cu, 40.2 per cent. Zn in Ag, 42.5 per cent. Cd in Ag and only 1.7 per cent. Cd in Cu.

It might at this stage be mentioned that when the atomic diameter of the solute atom happens to fall just inside the favourable range of the solvent atom the deductions tend to be somewhat unreliable. However, when we deal with the question of the solid solubilities of silver in copper, and of copper in silver, we find that each metal falls only just within the favourable range of the other; we are not, therefore, surprised to find the copper-silver equilibrium diagram showing that somewhat restricted solid solubility does occur in each instance.

Modifications. It should be noted that both of the solvent elements, copper and silver, are monovalent, i.e. they both have atoms in which there is only one outer-layer or valency electron, while the solute elements, zinc, magnesium, cadmium and beryllium, are all divalent, i.e. they all have atoms with two outer-layer or valency electrons. We shall soon be in a position to show how important in alloy structures these valency electrons can be; we must content ourselves for the moment, however, by stating that Hume-Rothery has examined the solid solubility of various metals in the divalent solvent magnesium, and has shown that the favourable size-factor principle may be equally well applied to magnesium alloys, typical of

those with excess of a divalent solvent. Recently Hume-Rothery has explained that, while good results may be obtained by considering the closest distance of interatomic packing as the atomic diameter, it is not really correct to express the atomic diameter as a single constant. He has therefore extended his theory by dividing metals into two groups, which he terms "open" metals and "full" metals. In "open" metals the interatomic distances are large compared with the diameters of the metallic ions, e.g. the atomic diameter of magnesium in a metallic structure is about 3.2\AA , while the diameter of the Mg ion is about 2.0\AA . In "full" metals the ions are relatively larger than the atomic diameters. This means that in "open" metals there are spaces between the ions, while in "full" metals the electron clouds of the individual ions are interpenetrating. These refinements do not, however, mean that the previous theory must be discarded; in fact, they have increased its value by enabling it to clarify a number of apparent difficulties.

Other Factors. It must now be emphasised that extended solid solubility is *not always found* when size-factors are favourable, since other factors may enter into the problem, and a discussion of these will follow. It has, however, been confirmed that a favourable size-factor is the first essential in deciding whether one metal may be expected to form extended solid solutions in another. Again, when size-factor restricts solid solubility it is usually found that solid solubility increases with rise of temperature, so that considerations of such combinations may result in the development of new precipitation hardening alloys, in which low solid solubility at ordinary temperatures is, of course, essential.

Valency Factor. We have already seen that when attempting to determine whether any two metals will, on alloying, form extended solid solutions, the first things to consider are the size-factors of the atoms concerned. It has been shown that when the ± 14 per cent. size-factor is unfavourable solid

solution will be restricted, but when the size-factor is favourable there is a probability—but no certainty—that solid solution will be extended. We must now look into the other factors which influence solid solubility.

It has already been mentioned that while atoms may be characterised by definite sizes their *properties* are largely governed by their respective outer-layer or valency electrons. We should not, therefore, be surprised to find that the other important influence is exerted by what may be called the outer-layer electron or *valency-factor*.

Effect of Increasing Valency of Solute. It has been found that *when size-factors are favourable extended solid solutions are most likely to be formed when the metals concerned have atoms with the same number of outer-layer electrons, i.e. when they have the same valency*. When size-factors are favourable and valencies unequal the extent of solid solubility will decrease as the difference between the respective valencies increases. To examine the effect of the valency-factor we may consider the extent of the solid solubility in copper (Cu), of the favourable size-factor but increasing valency metals, zinc (Zn), gallium (Ga), germanium (Ge) and arsenic (As), and in silver (Ag) of the corresponding favourable size-factor metals, cadmium (Cd), indium (In), tin (Sn) and antimony (Sb). The necessary atomic diameters and valency data (*vide* p. 61), and the results of experimental work on these alloys, as far as the primary solid solutions are concerned, are summarised in Tables IX (a) and (b).

The data show that increasing valency of solute has a marked effect in restricting solid solubility, and bring out the remarkable fact that the maximum solid solubilities of the divalent metals zinc and cadmium in copper and silver respectively are both about 40 atomic per cent., those of the trivalent metals gallium and indium are both about 20 atomic per cent., and those of the tetravalent metals germanium and tin are both about 12 atomic per cent.

TABLE IX (a).—DATA FOR SOLID SOLUBILITY OF SOLUTES OF INCREASING VALENCY IN COPPER AND SILVER

Element	Valency	Atomic Diameter †
Cu	1	2.55
Zn	2	2.75
Ga	3	ca. 2.7
Ge	4	2.79
As	5	—
Ag	1	2.88
Cd	2	3.04
In	3	3.14
Sn	4	3.16
Sb	5	3.23

† Goldschmidt's atomic diameter (co-ordination number 12), *vide* p. 60.

TABLE IX (b).—SOLID SOLUBILITIES IN COPPER AND SILVER OF SOLUTES OF FAVOURABLE SIZE-FACTOR AND INCREASING VALENCY

Solvent	Maximum Solubility of Solute (Atomic per cent.)			
Copper	38.4 Zn	20.3 Ga	12.0 Ge	6.9 As
Silver	42.5 Cd	20.0 In	12.2 Sn	7.2 Sb

Electron Concentration. This *quantitative* observation is so outstanding, and its bearing on the importance of the outer-layer or valency electrons is so great, that we must examine it in more detail. The solvent metals are in each case univalent, so that in the lattices of copper and silver each atom has one electron to donate to what we have called the electron paste or cloud (p. 25), so leaving the Cu^+ and Ag^+ ions to take up their lattice positions. When an atom of the univalent solvent is replaced by one of a divalent solute (e.g. Zn in Cu, or Cd in Ag), the solute atom brings with it *one extra electron*; similarly, trivalent solute atoms bring *two* extra electrons and quadri-valent solute atoms bring *three* extra electrons. It is thus obvious that while unfavourable size-factors may introduce

mechanical distortion of the solvent lattice, *increasing valencies of solutes can*, in a corresponding way, *extend and distort the lattice's electron cloud*. We are justified in supposing that electron cloud distortion cannot proceed indefinitely and that it must at some stage reach a limit. We would therefore expect to find that in the above series the maximum solid solubilities would vary inversely as the number of extra electrons introduced by the different solute atoms. The maximum solid solubilities of the different favourable size-factor solutes in the monovalent solvents copper and silver should thus be in the ratio 1 (divalent solute) : 1/2 (trivalent solute) : 1/3 (quadrivalent solute), although slight differences in size-factors would probably result in minor modifications of these proportions. Experimental results confirm the deductions, for the divalent solutes have respectively maximum solid solubilities of 40 atomic per cent. (e.g. Zn in Cu, 38.4 ; Cd in Ag 42.5) ; the trivalent metals have respectively maximum solid solubilities of the order of $40/2 = 20$ atomic per cent. (e.g. Ga in Cu, 20.3 * ; In in Ag, 20.0) ; and the quadrivalent metals have respectively a maximum solid solubility of about $40/3 = 13$ atomic per cent. (e.g. Ge in Cu, 12.0 ; Si—with a more favourable size-factor—in Cu, 11.6 ; Sn in Ag, 12.2 †).

Let us consider the maximum solid solubility, in copper and silver respectively, of the divalent solutes zinc and cadmium. For every 100 atoms of this solid solution there are 60 atoms of monovalent Cu or Ag and 40 atoms of divalent Zn or Cd, so that the total number per 100 atoms of electrons donated to the electron cloud is $(60 \times 1) + (40 \times 2)$, i.e. 140. Thus, in these extreme solid solutions, the number of electrons per atom—i.e. the electron concentration—is 1.4. It can be shown that the maximum solid solubility of the trivalent and quadrivalent

* Compare Al in Cu (aluminium bronze): maximum solid solubility, 20.4 atomic per cent.

† The very restricted solid solubilities of the pentavalent solutes As and Sb are due to the electrochemical factor (*vide* p. 74).

metals is also found when the electron concentration is also 1.4; e.g. maximum solid solubility of Al in Cu is about 20 atomic per cent., so that there are, per 100 atoms, $(80 \times 1) + (20 \times 3)$, i.e. 140 valency electrons. Again, the maximum solid solubility of tin in silver is about 12 atomic per cent., so that there are, per 100 atoms, $(88 \times 1) + (12 \times 4)$, i.e. 136 (approximately 140) valency electrons. It may therefore be concluded that for solid solutions in copper and silver the maximum solubility of the metals of Groups IIB, IIIB and IVB, with favourable size-factors, is found when the electron concentration is 1.4 (*vide* p. 118).

It might be useful to give here a general rule for calculating electron concentration, as follows: Electron concentration = $\underbrace{V(100 - x) + vx}_{/100}$, where x atomic per cent. of the solute metal, of valency v , is in solid solution in a solvent metal of valency V .

Effect of Increasing Valency of Solvent and of Decreasing Valency of Solute. We have so far confined our attention to solid solution (when size-factors are favourable) in the univalent and noble metals copper and silver. In order to consider mainly the effect of altering the valency of the solvent, and, incidentally, of altering the electrochemical character of the solvent, we may now discuss the solid solutions in the divalent electropositive metal magnesium of the favourable size-factor metals silver, cadmium, indium, tin and antimony. We find * that the maximum solid solubilities are about (in atomic percentages) Ag in Mg 5, Cd in Mg 100—i.e. continuous solid solubility, In in Mg 20, Sn in Mg 5, and Sb in Mg 0. The general effect of increasing valency of solute atom in restricting solid solubility is the same as before; compare, e.g., the wide solid solubility of divalent cadmium in magnesium with the fairly restricted solid solubility in the same solvent of indium, a trivalent metal.

* Hume-Rothery, "Researches on the Structure of Alloys," p. 6.

Two new effects are, however, encountered. Thus, there is extremely restricted solid solubility of univalent silver in divalent magnesium, while the alloys of magnesium with tin and antimony are of entirely different types, and are, indeed, characterised by the presence of stable intermetallic compounds. The latter observation suggests that one of the causes of the formation of stable intermetallic compounds (*vide* p. 85) is the presence, in an alloy, of a strongly electropositive metal, for example, magnesium, and an electron-deficient metal, like antimony.

We have seen that the first consideration in connection with the possibility of extended solid solubility is the question of the relative sizes of the atoms of the metals concerned, and that when sizes are favourable the next determining factor is the relative valencies of solvent and solute. We find that the more the valency of the solute differs from that of the monovalent solvent, the more restricted the solid solubility becomes. When, however, the noble metal solvent is replaced by a divalent and strongly electropositive metal like magnesium, two striking observations are made: (a) Solutes of lower valency than the solvent show only restricted solid solubility even when size-factors are favourable; and (b) The more the electrochemical properties of the solvent and solute differ the greater is the tendency to form intermetallic compounds in preference to solid solutions. These effects are both important.

Effects of reducing Electron Concentration. The restricted solid solubility of a solute of lower valency is not too difficult to explain if, first, we deal with an extreme case, e.g. the mutual solid solubilities of silicon and copper. The size-factors are both favourable (Cu, atomic diameter, 2.55\AA ; Si, atomic diameter, 2.35\AA), and from our previous work we should expect copper to be able to take into solid solution about as many atoms per cent. of quadrivalent silicon as it does of quadrivalent tin, i.e. about 10 atomic per cent. The actual figure for the maximum solid solubility of silicon in copper is

11.6 atomic per cent.—and our assumption is therefore completely justified. Once again it would seem that the lattice of the solid solution of maximum concentration is characterised by an electron concentration of 1.4; in other words, the electron cloud of the copper lattice may be enlarged to that of the saturated solid solution in the ratio of 1 : 1.4. Conditions must, however, be very different when the presence of solute atoms of relatively lower valency brings about lattice *electron impoverishment*. It is under such conditions that silicon would be the solvent and copper the solute. The silicon lattice—the solvent lattice—is of the tetrahedral cubic or diamond type, and is covalent in character. Each silicon atom, with its four valency electrons, is surrounded by four others similarly equipped, so that, by the formation of covalency links, the stable electron octet is completed for each atom of the lattice. The introduction of a monovalent copper atom in place of one of silicon means a deficiency of three electrons for each copper atom added. This would obviously upset the stability of the silicon lattice to a considerable extent, and it is therefore understood that solid solution of copper in silicon should be extremely restricted; in fact, this is found to be so, for the published data show that it cannot be greater than 2 atomic per cent. It is for these reasons that: (i) Metals with covalent type crystals never form solid solutions containing appreciable amounts of metals with lower valencies; (ii) These metals may form extended solid solutions with metals of the same group: e.g. antimony and bismuth form alloys showing continuous solid solubility; (iii) Metals like magnesium are only able to hold in solid solution restricted amounts of solute metals like silver and gold of lower valency. It might be mentioned here that magnesium can hold in solid solution about 20 atomic per cent. of lithium (monovalent), but this is exceptional and is an example of the well-known anomalous behaviour of the elements of the first period, viz. lithium, beryllium, boron, carbon, nitrogen, oxygen and fluorine.

Solid Solubility when Size-Factors are favourable and Valencies the same. Having dealt with the effects on solid solubility of both higher valency and lower valency solutes, we may now pass on to deal with the structures of those alloys in which the metals have *favourable* size-factors and the *same* valency. We may assume that under such conditions the introduction of atoms of the one metal into the lattice of the other will bring about the minimum distortion in both the ion lattice and the electron cloud, so that everything favours extended solid solution. Data for such alloys are given in Table X.

TABLE X.—SOLID SOLUBILITIES WHEN SIZE-FACTORS ARE FAVOURABLE AND VALENCIES THE SAME

<i>Alloy</i>	<i>Difference of Atomic Diameter. Per cent.</i>	<i>Type of Equilibrium Diagram</i>		
Silver-Copper	12.5	Restricted solid solutions. Eutectic type.		
Silver-Gold	0.1	Continuous solid solution.		
Magnesium-Cadmium	8.0	„	„	„
Arsenic-Antimony	12.2	„	„	„
Antimony-Bismuth	7.5	„	„	„
Molybdenum-Tungsten	0.4	„	„	„
Nickel-Platinum	10.0	„	„	„

The data seem to confirm the idea that atoms of identical size and valency can be substituted for one another with much less disturbance than occurs when either the atomic diameters or the valencies are different. The most favourable condition for wide solid solution is, therefore, that the atoms should be of nearly the same size and that they should have the same number of outer-layer or valency electrons. It must, however, be noted that the satisfaction of the latter condition does not, of necessity, mean that the metals concerned *must* belong to the same periodic table group. In fact, continuous solid solubility does occur in many binary alloys of the transitional elements with one another and with the elements of Group IB—copper, silver and gold—provided, of course, that the size-factors are

in each case favourable. We might well conclude this section by stating that *solid solution passes from "extended" to "restricted" as we move from alloys in which size-factors are favourable and valencies the same to those in which size-factors are favourable and valencies different and then to those in which not only are valencies different but size-factors are also unfavourable.* The first and third of these conditions represent respectively the most favourable and the least favourable for the formation of solid solution.

The Electrochemical Factor. We now come to the question of the last main consideration involved when dealing with the problem of solid solution and solid solubility. This is the question of the influence of what Hume-Rothery calls the *electrochemical factor*. This denotes differences in the two alloying metals based on their electrochemical characteristics. Examples of the influence of this electrochemical factor have already been encountered in the alloys of electropositive magnesium on the one hand, and electro-negative antimony and bismuth on the other (p. 70). *A high electrochemical factor—i.e. considerable difference between the electrochemical properties of the metals concerned—has a strong tendency to restrict the formation of solid solutions and to favour the formation of intermetallic compounds.* Solid solubility which is restricted at ordinary temperatures by a high electrochemical factor usually increases with rise of temperature, for two reasons. First, increase of temperature means greater thermal oscillation of the atoms of a given lattice, thus facilitating the accommodation of new atoms; and, second, it also usually favours the partial dissociation of intermetallic compounds, so that it favours the transfer of atoms from such compounds to solid solution. The same tendency is encountered in ternary alloys, particularly when, as in duralumin type alloys, the compound—in this case Mg_2Si —is formed between solute atoms. Careful consideration of size-factor and electrochemical factor should therefore prove most helpful in developing new precipitation hardening alloys,

in which conditions may be so arranged as to cause precipitation of extremely fine compound particles inside the crystal grains of the solvent metal. It must, however, be kept in mind that if a homogeneous structure is required at the solution heat-treatment temperature, the solute atoms must not have *too* unfavourable size-factors or be *too* strongly electronegative with regard to the solvent. It may be noted in this connection that although it is usual to find that solid solubility decreases with fall of temperature, there are a few exceptional cases in which the reverse holds good, e.g. in the copper-zinc and the copper-aluminium systems. A possible explanation of this anomaly may be found in the fact that the solid solubility curve represents an equilibrium between one phase and another, and its exact form must therefore depend on the nature of the second phase and on the effect of temperature on the equilibrium.

Effects of Solute on Mechanical and other Properties. To conclude this discussion we will briefly refer to the effects of solute atoms on (a) the mechanical and electrical properties of the solvent, and (b) the depression of the liquidus and solidus curves. (a) A solid solution is usually harder and stronger than the solvent metal and has a higher electrical resistance. Careful measurement of the lattice constants of solid solutions have shown that, with increasing amounts of solute, there is a regular increase in lattice distortion and in the mechanical property of hardness; it has, in fact, been possible to correlate hardness with extent of lattice distortion. Electrical resistance measurements on solid solutions in silver indicate that the increase of resistance per 1 atom per cent. of solute is directly related to the valency of the solute and is proportional to $(v-1)^2$, v being the valency of the solute atom. (b) The careful experimental study of the previously described series of alloys of copper and silver has shown that the depression of the liquidus and solidus by, in each case, 1 atom per cent. of solute are respectively proportional to the valency of the solute and to the square of the valency of the solute. The

depression of the solidus curve also increases with difference of size-factor and with difference of valency, and the solidus curve is more affected than the liquidus curve in each case. With increasing difference between the atomic diameters of the solvent and solute, and between their valencies, the solidus curve falls more steeply, and the contrast between the depression of the liquidus and of the solidus becomes more and more marked. It is well known that a large freezing range is undesirable, in that it causes segregation during the solidification of castings. It has therefore been suggested that if in a binary system the freezing range is unduly great, because, for example, the solute atom is larger than that of the solvent, then it may be possible to diminish segregation in a casting of the alloy by adding a smaller atom of the same valency.

CHAPTER VII

ATOMIC ARRANGEMENT IN SOLID SOLUTIONS

Disordered Solid Solution. The first assumption usually made when considering the arrangement of the atoms in substitutional solid solutions is that the solute atoms take up, in a completely random way, the positions of some of the solvent atoms. It is this type of disordered substitutional solid solution which is indeed most commonly found, although such is not always the case, for in one or two important, though apparently exceptional, alloy systems there exist, under equilibrium conditions, solid solutions in which the solute atoms themselves are arranged in a perfectly regular way. Under such circumstances the solute atoms form what might be termed a "lattice within a lattice." It is with these that we shall have to deal in some little detail. Meanwhile it might be stated that since the usual tendency is for the introduction of solute atoms to cause at least some distortion of the solvent lattice, it is natural to assume that, whenever possible, the distortion effect will be evened out by the solute atoms taking up positions as far away from each other as the conditions will allow. Such considerations lead to the conclusion that, under favourable conditions, solute atoms *may* take up positions so that each one has only a limited number of neighbours of its own kind situated at points regularly arranged in space around it. The necessary favourable conditions, as will be seen later, are rarely found in practice, but, when they do exist, what is described as a *superlattice* is produced (p. 63). A *superlattice* consists of a lattice of solute atoms inside the lattice of the solvent, and is distinguished from a disordered solid solution by the fact that, in the latter, the solute atoms are arranged, completely at random, in the one and only lattice of the parent metal. In those alloy systems

in which superlattices may be expected to form—and they are at present thought to be comparatively few—it is reasonable to believe that the distortion effect (the ultimate cause of superlattice formation) would gradually disappear as the temperature rises and the thermal oscillations increase. Hence, alloys in which superlattice-type solid solutions are formed at low temperatures would be expected to transform at higher temperatures to solid solutions of the normal disordered substitutional type; it might even be possible to find in such alloys disordered solid solutions after quenching from relatively high temperatures, while slow cooling or annealing at low temperatures would produce solid solutions of the superlattice type. Careful X-ray study of suitable alloy systems has, within recent years, conclusively shown that these phenomena occur as predicted.

Ordered Solid Solution. The traditional example of what is now known to be due to transformation in solid solution of a disordered lattice into an ordered superlattice occurs during the slow cooling of a wide range of copper-gold alloys, in which it may be noted that size-factors are only just within the favourable range and the valencies happen to be the same. About thirty years ago a careful examination of the effect of slow cooling as compared with quenching (from just below the solidus) on the mechanical and electrical properties of copper-gold alloys was made and some remarkable results were obtained. The equilibrium diagram of this system (p. 96) shows that the alloys are characterised by continuous solid solubility, as would be expected in view of our previous discussions. It is usual to find that, when the mechanical or electrical properties of solid solution-type alloys are plotted against composition, the curves show increasing hardness, strength and electrical resistance, and are normally perfectly continuous. In fact, breaks in such curves were at one time thought to indicate the formation of an entirely new phase. It will be seen from Fig. 24 that this normal behaviour is shown by the *quenched*

copper-gold alloys but *not* by the *slowly cooled* ones, and that the very sharp minima points on the curves for the slowly cooled (equilibrium) alloys occur in those containing respectively 3 atoms of copper to 1 of gold, and 1 atom of copper to 1 of gold. This remarkable behaviour was thought to indicate the formation, in the slowly cooled alloys and at

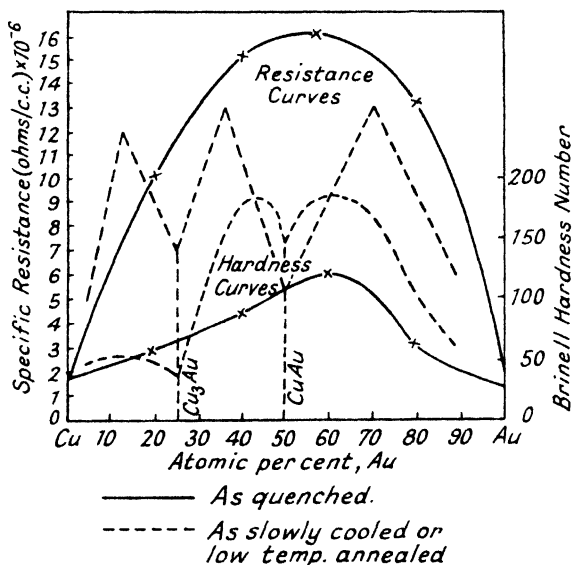


FIG. 24.—Effect of Composition on Electrical Resistance and Hardness of Copper-Gold Alloys: (a) Quenched. Disordered-Solid Solution, (b) Slowly Cooled. Ordered-Solid Solution.

relatively low temperatures, of the intermetallic compounds Cu_3Au and CuAu , respectively. Modern X-ray work indicates that what really does happen is that, at the lower temperatures (where conditions are more favourable), the ordinary disordered solid solutions break down, producing superlattices, which, when complete, may be represented by formulæ once thought to be confined to actual compounds.

Order and Disorder in Copper-Gold Alloys. The way in which the copper and gold atoms are arranged in the slowly cooled alloy containing 75 per cent. Cu and 25 per cent. Au is shown in the lattice unit of Fig. 25, in which the black circles represent copper, and the white ones gold, atoms. It is seen that the lattice unit behaves as though it contains $6 \times \frac{1}{2}$ atoms of copper and $8 \times \frac{1}{8}$ atoms of gold, i.e. three atoms of copper and one of gold, and this corresponds to the formula Cu_3Au . It will be noted that this particular alloy, in the slowly cooled condition, shows none of the properties (mechanical) generally associated

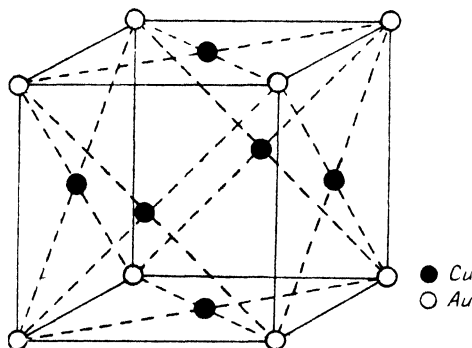


FIG. 25.—Complete Ordered-Solid Solution, containing 75 Atomic per cent. Cu and 25 Atomic per cent. Au.

with intermetallic compounds ; thus, as shown by Fig. 24, its hardness is no greater than that of copper itself. However, its formation and superlattice structure do bring out the important fact that *the fundamental difference between solid solutions and intermetallic compounds is by no means as great as was once imagined*. The X-ray diffraction patterns of annealed specimens of copper and Cu_3Au are shown in Fig. 26. It should, of course, be noted that the lattice unit of this 75 per cent. Cu-25 per cent. Au (atomic per cent.) *solid solution* at high temperatures has its copper and gold atoms in the same 3 : 1 proportions, but they are then arranged entirely at random.

The 50-50 atomic per cent. alloy in the slowly cooled condition also has an ordered or superlattice structure which corresponds to the formula CuAu , but in this case the face-centred lattice unit must behave as though it contains two atoms of copper and two of gold. In order to satisfy these conditions, not only are the eight corner atoms gold, but also another two, e.g. the top and bottom face-centred atoms, are gold, leaving the remaining four face-centred positions to be occupied by copper atoms. The superlattice now consists of alternative layers of gold and copper atoms, and, while it remains face-



FIG. 26 (a).—X-Ray Diffraction Pattern for Annealed Copper.



FIG. 26 (b).—X-Ray Diffraction Pattern for Annealed Cu_3Au , containing 75 Atomic per cent. Copper and 25 Atomic per cent. Gold, Showing Change of Lattice Dimension but no Change of Lattice Form (i.e. no Change of Phase).

centred, the difference in size of the two atoms is probably responsible for the fact that the superlattice is a distorted cubic one. It is thus correctly described as face-centred tetragonal. The distortion is, however, small, and the axial ratio of the tetragon is very nearly equal to one. This probably accounts for the greater hardness (Fig. 24) of the CuAu superlattice structure. Once again, heating to temperatures near the solidus results in the complete breakdown of the superlattice and the arrangement of the copper and gold atoms becomes entirely disordered, as indicated in Fig. 34 (a) (p. 96).

Order and Disorder in Iron-Aluminium Alloys. A most valuable contribution to the X-ray examination of superlattice structures was made in their study of the iron-aluminium alloys by Bradley and Jay in 1932. The atoms of these metals have diameters which are such that they fall only just within the favourable range for the formation of wide solid solution of aluminium in iron. The lattice of the solvent metal, iron, is in this case body-centred cubic, and eight adjacent lattice units

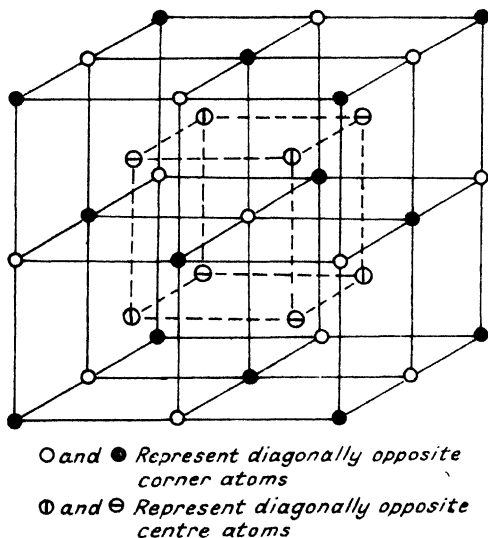


FIG. 27.—Superlattice Formation in Iron-Aluminium Alloys.

are shown in Fig. 27, in which certain alternative lattice positions are indicated. The results of the experimental work showed that :

(a) Those alloys containing up to about 18 atomic per cent. aluminium have random arrangement solid solution lattices, in both quenched and slowly cooled conditions. In these alloys the solute atoms (aluminium) are evenly distributed amongst all four possible positions.

(b) As the aluminium content increases the slowly cooled alloys are now found to have superlattice structures in which the aluminium atoms tend to concentrate in the \ominus positions. In fact, with 25 atomic per cent. aluminium all of these positions may be filled, and, to all intents and purposes, no aluminium atoms are found in any of the other positions after slow cooling. The lattice unit then behaves as though it contains, taking the average of two adjacent lattice units, $\frac{1}{2} \times 1$ atom of aluminium + $\frac{1}{2}(16 \times \frac{1}{8} + 1)$ atoms of iron—i.e. half an atom of Al to one and a half atoms of Fe. This alloy may therefore have, under suitable conditions, a superlattice structure corresponding to the formation of the compound Fe_3Al .

(c) With further additions of aluminium the solute atoms gradually replace the iron atoms at the centres of the previously aluminium-free lattice units. In the alloy with 37.5 atomic per cent. of aluminium, one-half of the solute atoms are in the \ominus position and the other half in the \oplus ; none of them is found at the cube corners, and this applies whether the alloys are quenched or annealed. With 50 atomic per cent. aluminium, all the cube centre positions are taken by aluminium atoms, and each lattice unit then contains $8 \times \frac{1}{8}$ atoms of iron and 1 atom of aluminium—corresponding with the formula FeAl .*

Superlattice Formation : General Conclusions. It has thus been experimentally established that the solute aluminium atoms at first keep as far away from each other as possible, and, as the concentration of the solid solution increases, they then take up positions (under suitable conditions), first at a distance of $a \cdot \sqrt{2}$, and then at a distance a , from each other, a being the lattice parameter. They are extremely unlikely to take up the "possible" positions separated only by the dis-

* It has recently been stated that iron-aluminium alloys, containing up to about 20 per cent. aluminium and about 1 per cent. each of nickel and chromium, compare in appearance with high chromium nickel steels, and have been produced in sheet form. These alloys are brittle "as cast," but may be made ductile by low-temperature annealing. (*Vide Journal of the Royal Society of Arts*, Vol. XCII, No. 4663, p. 240.)

tance $a \cdot \sqrt{3}/2$. Again, superlattices do not form, or else are extremely unstable, in dilute solid solutions—when areas of lattice distortion are, even in a random arrangement, unlikely to be near together. The stability of a superlattice increases with decrease of solute-interatomic distance, and also with increased differences of atomic diameters. Both of these factors tend to cause internal strain, and it is superlattice formation which might reduce it. Indeed, it is because of the second factor that superlattice formation is relatively uncommon, for, when atom sizes vary, the possibility of solid solution, to a degree sufficient for superlattice formation, becomes more and more remote.

It may be noted, in conclusion, that superlattice formation provides a satisfactory explanation of the well-known but imperfectly-understood $\beta \rightarrow \beta'$ phase transformation in the brasses.

CHAPTER VIII

INTERMETALLIC COMPOUNDS

Properties and Composition. Intermetallic compounds are well known for their extreme hardness and brittleness. Indeed, few of them are, as such, of any practical value, although their importance, when present in relatively small quantities in heat-treatable alloys like steel and duralumin, and in bearing metals, can hardly receive sufficient emphasis. They are generally relatively good conductors of electricity and show more or less pronounced metallic characteristics. Most intermetallic compounds should therefore have, at least to some slight degree, characteristic lattices in which the formation of a "metallic" valency electron cloud may, under suitable conditions, be possible. Such a state of affairs is, of course, quite impossible in "normal" chemical compounds, which we have already seen (p. 25) may be either ionic or homopolar. In the ionic compound the valency electrons of one atom or group of atoms are entirely transferred to another atom or group of atoms, thus producing the well-known electrovalency bonds; in homopolar compounds, on the other hand, the atoms are held together by electrons which are shared so that they are *all* needed to maintain the stability of the compound itself. It is, in fact, this complete transferring or sharing, as the case may be, of valency electrons which provides the mechanism of *normal* chemical combination based on the well-known laws of valency. In ordinary chemical compounds, therefore, there are no "free" electrons, and in such compounds there is no valency electron lattice cloud. Some intermetallic compounds obey the valency laws, e.g. those with the formulæ Mg_2Si , Mg_2Sn , Mg_3Sb_2 , etc.; we may expect to find that they, and others like them, will behave more like ordinary chemical

compounds, with their "tied" valency electrons, than like metals with electron cloud lattices.

The vast majority of intermetallic compounds, however, do not obey the ordinary valency laws, and have such formulæ as AgMg , Cu_5Si , Cu_5Zn_8 , $\text{Na}_{31}\text{Pb}_8$, CuZn_3 , etc. While it is only within recent years that Hume-Rothery and others have been able to offer rational explanations of the formulæ, and, indeed, structures, of these extraordinary-valency compounds, it might be mentioned that we should not *expect* compounds, which are metallic in structure and properties, to have formulæ which suggest that the valency electrons of the atoms concerned are completely "tied" in chemical combination, and are therefore unable to assist in, for example, the conduction of electricity.

Chemical and Intermetallic Compounds. When we attempt to answer the question as to whether or not we may regard intermetallic compounds as actual chemical compounds we must first of all decide as to what we mean by the chemical bonding of atoms. If, on the one hand, we consider chemical forces as those which are brought about either by the complete transference of valency electrons (electrovalency) or by their complete sharing (covalency), then we have to regard intermetallic compounds as being linked by forces of the same physical nature as those involved in metals. On the other hand, we may adopt the alternative interpretation and consider all cases of atomic linkage, whether ionic, homopolar or metallic, as fundamentally chemical in character; in this case we have types of chemical combination which differ only in degree as we pass from electrovalent and homopolar compounds to the interatomic, or interionic, linking of metals and alloys, and intermetallic compounds then take their places as intermediate in character. Regarding them from the latter viewpoint we might expect to find that some intermetallic compounds will show structural and property characteristics of "ordinary" chemical compounds, while other intermetallic

compounds should have structures like, and properties resembling, those of pure metals. These expectations are, in actual fact, found to be justified, for "normal valency" intermetallic compounds are more like ionic substances—for example, sodium chloride—than metals, while "abnormal valency" intermetallic compounds have many of the properties which we associate with metals. Chemical combination may thus be regarded as responsible in different ways for the formation of (a) homopolar compounds, (b) ionic compounds, (c) "normal valency" intermetallic compounds, (d) "abnormal valency" intermetallic compounds, and, finally (e) metals and alloys. This gives a convenient method of classifying intermetallic compounds, and we shall therefore proceed to discuss the "normal valency" type first.

Composition of Normal Valency Intermetallic Compounds.

It has already been mentioned that normal valency intermetallic compounds are like ionic compounds. They have, for example, relatively high melting-points. Thus, the melting-point of sodium chloride (801°C.) is of the same order of magnitude as the melting-points of the compounds: Mg_2Sn (780°C.), Mg_3Sb_2 ($1,228^{\circ}\text{C.}$), Mg_3Bi_2 (823°C.) and Zn_3Sb_2 (570°C.).

It will be remembered that ionic compounds are formed by the electrovalent combination of elements, the atoms of which have a few outer-layer electrons in excess of an inert gas structure, with elements whose atoms have outer layers which need corresponding numbers of electrons in order to acquire a stable inert gas structure. The most stable ionic compounds are therefore formed between the strongly metallic elements on the left-hand side of the periodic table and the definitely non-metallic elements of the extreme right. There are, however, on the right-hand side of the periodic table a number of elements with atoms which are deficient in outer-layer electrons but which are not strongly non-metallic in character, e.g. sulphur, selenium and tellurium (Group VI); phosphorus, arsenic, antimony and bismuth (Group V); and carbon, silicon,

germanium, tin and lead (Group IV). *It is the combination of these electron-deficient elements with electron-excess metals of Groups I and II which results in the formation of normal valency intermetallic compounds*, the combination mechanism being usually akin to electrovalency and the metals (of the early groups) providing the necessary electrons required by the right-hand side metalloids and non-metals. It will also be remembered that their general chemical properties suggest that in a given group (A) at the left-hand side of the periodic table the greater the atomic number the more electropositive is the metal: e.g. potassium is more electropositive than sodium, and sodium is more electropositive than lithium; similarly, or rather conversely, for the elements of the right-hand groups the smaller the atomic number the more electronegative are the elements of any one particular group: e.g. sulphur is more electronegative than selenium, and phosphorus is more electronegative than arsenic, and arsenic more electronegative than antimony.

We are now able to state that normal valency intermetallic compounds tend to form between all relatively low valency metals on the one hand, and such high valency elements as sulphur and selenium (Group VI), phosphorus, arsenic, antimony and bismuth (Group V), and silicon, germanium, tin and lead (Group IV) on the other. Further, *the tendency towards the formation, and the stability when formed, of such normal valency intermetallic compounds will be greatest when the metals are strongly electropositive and their opposite numbers are markedly electronegative*. Thus, the strongly electropositive metal, magnesium, forms the following normal valency compounds with the elements previously mentioned: (a) MgS and MgSe ; (b) Mg_3P_2 , Mg_3As_2 , Mg_3Sb_2 and Mg_3Bi_2 ; and (c) Mg_2Si , Mg_2Ge , Mg_2Sn and Mg_2Pb . In each of the respective series it is found that the first compound, i.e. the one of magnesium with the most electronegative element, has the highest melting-point and is the most stable, while the last in each series has the lowest melting-point and is the least stable of that series.

Structures of Normal Valency Intermetallic Compounds.

When we discuss the actual crystal structures of these normal valency type intermetallic compounds we find once again close resemblances between them and their truly ionic or homopolar counterparts. The crystal lattices of ordinary chemical compounds of formulæ XY , X_3Y_2 and X_2Y are very similar to those of the corresponding normal valency intermetallic compounds with the same formulæ. We cannot, of course, deal here with the lattice structures of ordinary inorganic compounds in detail, and must content ourselves with a brief reference to those typical inorganic compounds the structures of which are

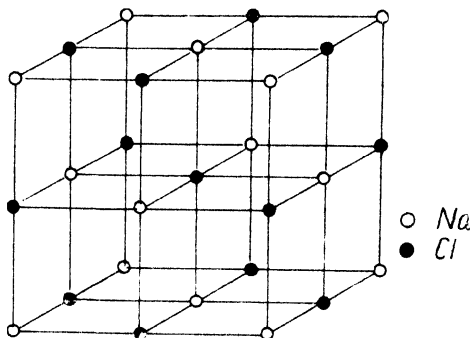


FIG. 28.—Sodium Chloride Lattice.

closely related to those of the normal valency intermetallic compounds. Perhaps the simplest ionic lattice is that of sodium chloride, shown in Fig. 28, but only a few normal valency intermetallic compounds, e.g. $MgSe$ and $CaTe$, have their atoms arranged in this way. A more common prototype ionic lattice is that found in the well-known calcium fluoride (CaF_2) structure, Fig. 29, in each unit cube of which there are twice as many non-metal as metal atoms. A modified lattice, said to be anti-isomorphous with that of fluorite (CaF_2), is formed in those intermetallic compounds like Mg_2Si , Mg_2Sn and Mg_2Pb ,

in which there are twice as many metal atoms as metalloid atoms, the typical compound lattice being then as shown in Fig. 30, the dark circles then representing Mg atoms and the

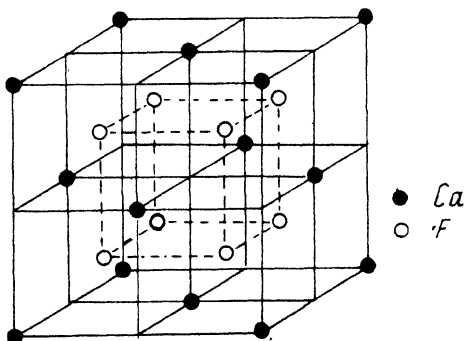


FIG. 29.—Calcium Fluoride Lattice.

light ones the other element of the compound. Those normal valency intermetallic compounds which have crystal lattices of the NaCl or CaF_2 types generally have relatively high specific

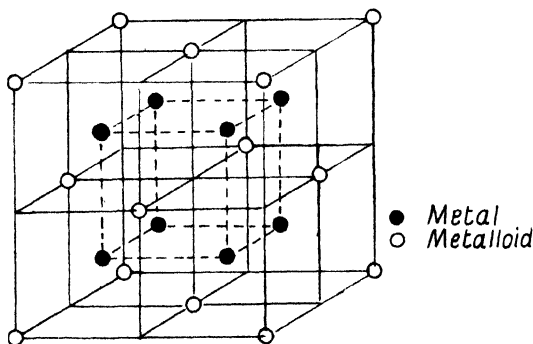


FIG. 30.—The Mg_2Si Lattice.

resistances and behave more like ionic compounds than metals, and thus also are characterised by relatively high melting-points.

Another type of lattice—this time of the homopolar class—found in normal valency intermetallic compounds is the tetrahedral cubic or adamantine lattice, which, when all the atoms are carbon atoms, occurs in the diamond, as shown in Fig. 31. This lattice is also present in crystals of the other tetravalent elements, silicon, germanium and grey tin. In all of these elements the atoms have four outer-layer or valency electrons, each of which contributes to the formation of the four tetrahedral homopolar valency bonds. The adamantine type lattice may also be found in compounds between two atoms, provided that their *average* number of valency electrons is also four. Thus, it occurs in

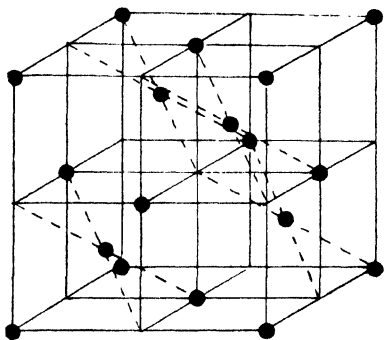


FIG. 31.—The Diamond Lattice.

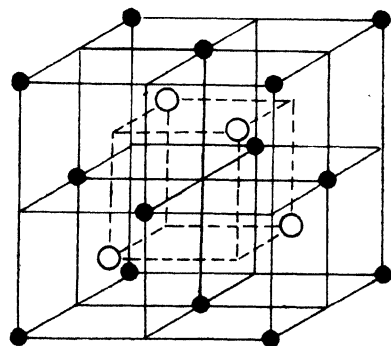


FIG. 32.—The Zinc Blend Lattice.

CdS , AlAs and AlSb , and in these the bonding is therefore homopolar rather than ionic in character.

The only other important lattice as far as the normal valency

the well-known zinc blend— ZnS —in which the Zn atom has two valency electrons and the sulphur atom has six, the average number of valency electrons being four per atom. The zinc blend lattice (Fig. 32) is thus found in such compounds as

intermetallic compounds are concerned is the nickel arsenide type, shown in Fig. 33. This is a layered type of structure which is formed in many of the XY compounds of the transitional elements like chromium, manganese, iron, cobalt, nickel and copper with metalloids like sulphur, selenium and tellurium, and arsenic, antimony and bismuth. Some typical nickel arsenide type intermetallic compounds are CoS, FeS, NiS, FeSn, CuSn, NiSn and MnAs. The actual interatomic bonding in these compounds seems to show characteristics intermediate between those of ionic and homopolar linkages.

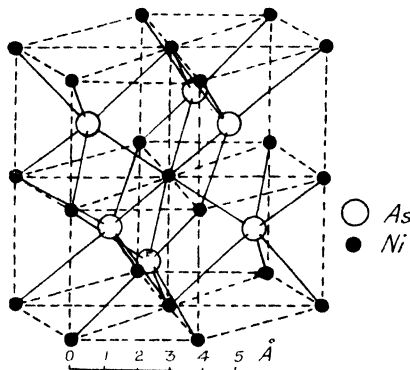


FIG. 33.—The Nickel Arsenide Lattice.

Abnormal Valency Inter-metallic Compounds. We have seen that *normal valency compounds* are generally formed during the alloying of “electron excess” metals, of Groups I and II of the periodic table, with “electron deficient” elements of Groups IV, V and VI. Such compounds resemble, in structure and properties, true chemical

compounds, and the metal and metalloid atoms are bound by linkages which are either of the ionic or homopolar types. The tendency towards the formation, and the stability when formed, of these normal valency compounds both appear to be greater the more electropositive the metal and the more electronegative the metalloid; the most stable compounds are formed by the higher atomic number metals with the lower atomic number metalloids. In the case of the metal atoms, the farther the valency electrons are away from the positive nucleus the more easily are they given up, leaving positive ions, and, in the case of the metalloid atoms, the

nearer the outer shell to the nucleus the more readily are electrons absorbed.

We have mentioned that *abnormal valency intermetallic compounds* are different, in that they show greater resemblances to metals than to ordinary chemical compounds; they possess, for example, relatively high electrical conductivity. This has led to the suggestion that such compounds are characterised by electron cloud metallic type lattices; they might therefore be expected to form during the alloying of two or more electron-excess metals, whether they are found in the early groups of the periodic table or whether they belong to the transition series metals. It is also reasonable to suppose that the tetra-valent elements might, under different conditions, give rise to both types of compound since they may behave as possessing either electron-excess or electron-deficient outer-layer shells. In order to examine the compositions and structures of abnormal valency intermetallic compounds we must therefore deal with those alloy systems which are formed when both of the constituent metals have atoms with only a small number of outer-layer valency electrons. We may, in fact, expect to find abnormal valency intermetallic compounds in some of the alloy systems in which the constituent metals are either found in Groups I, II, III (and, possibly, IV), e.g. copper, silver, gold, zinc, magnesium, cadmium, aluminium, silicon, tin, lead, or in the well-known transition series, e.g. chromium, manganese, iron, cobalt, nickel, molybdenum, tungsten, platinum, etc. The number of possible alloy combinations is now very much larger than it was under the conditions previously described for normal valency intermetallic compounds. We are not then surprised to find that the number of abnormal valency intermetallic compounds is greatly in excess of the corresponding number of normal valency ones.

It should be noted that not all of the possible alloy combinations suggested above will yield intermetallic compounds. We have seen, for example, that atoms with favourable size-

factors and the same number of valency electrons usually form continuous solid solutions, and under such circumstances cannot, of course, yield intermetallic compounds. We must not, however, jump to the opposite conclusion that these intermetallic compounds will be formed only when the atoms differ widely in size. There are, in fact, very good grounds for believing that one of the conditions necessary for the formation of abnormal valency intermetallic compounds is that the size-factors should be favourable. This, in turn, suggests, since similarity of valency would favour solid solution, that *these compounds are probably formed between relatively low valency metals when size-factors are favourable and valencies different.*

When we compare, for example, the ordinary per cent. by weight equilibrium diagrams of the alloys of monovalent copper with, first, divalent zinc, second, trivalent aluminium, and, third, tetravalent tin, we find that each system is characterised by similar α , $\alpha + \beta$, β , $\beta + \gamma$, γ , etc., phase areas. We have already noted that the range of α -solid solution decreases with increasing valency of solute, and that the maximum solid solubility, in each case, occurs at an electron concentration of 1.4 (p. 69).

Equilibrium diagrams plotted on an atomic per cent. base show that the β -phases all occur in the regions near abnormal valency intermetallic compounds, and are found respectively in the neighbourhood of 50 atomic per cent. zinc, of 25 atomic per cent. aluminium, and of 16.7 atomic per cent. tin (Fig. 34). This suggests that the different β -phases are based on the *apparently unrelated* intermetallic compounds CuZn , Cu_3Al and Cu_5Sn .

Hume-Rothery Rules. It was from observations like these that Hume-Rothery was able to develop his Intermetallic Compound Rules (1926). He showed that *the above, and other, β -phase abnormal valency intermetallic compounds*, have one common characteristic—they *all have three electrons to every two atoms*. Thus, in CuZn the one copper atom provides one electron and the other atom—zinc—supplies two, so that the

electron : atom ratio is 3 : 2 ; similarly, in Cu_3Al the four atoms provide the electron cloud with three electrons (one from each copper atom) and another three (from the aluminium atom), so that the electron : atom ratio is 6 : 4, i.e. 3 : 2 ; again, in Cu_5Sn the five copper atoms donate five and the one tin atom four electrons, so that the electron : atom ratio is 9 : 6, i.e. 3 : 2. So much for the β -phase.

It is reasonable to assume that if the formation of the β -phase type of abnormal valency intermetallic compounds requires a certain definite electron : atom ratio the other intermediate phases should also be based on similar ratios. Such is indeed the case, and we may extend our discussion of the Hume-Rothery Rules by considering the other phases of the copper-zinc, copper-aluminium and copper-tin systems. We find, for example, that the γ -phases occur near the compositions of 61.6 atomic per cent. zinc, 30.8 atomic per cent. aluminium and 20.5 atomic per cent. tin, respectively, which correspond to the compounds Cu_5Zn_8 , Cu_9Al_4 and $\text{Cu}_{31}\text{Sn}_8$ (Fig. 34). The " γ " electron : atom ratio is seen to be 21 : 13, as follows :

Cu_5Zn_8 contains $(5 \times 1) + (8 \times 2) = 21$ electrons to 13 atoms ;

Cu_9Al_4 contains $(9 \times 1) + (4 \times 3) = 21$ electrons to 13 atoms ;

$\text{Cu}_{31}\text{Sn}_8$ contains $(31 \times 1) + (8 \times 4) = 63$ electrons to 39 atoms,
i.e. 21 electrons to 13 atoms.

The next "electron : atom ratio" abnormal valency intermetallic compounds—they are called "electron compounds" now—are found in the ϵ -phases, in the region of the compounds CuZn_3 and Cu_3Sn (the corresponding copper-aluminium compound would be Cu_5Al_3 —its counterparts, Ag_5Al_3 and Au_5Al_3 , are known). These electron compounds are, once again in common, characterised by an electron : atom ratio of 7 : 4, as follows :

CuZn_3 contains $(1 \times 1) + (3 \times 2) = 7$ electrons to 4 atoms ;

Cu_3Sn contains $(3 \times 1) + (1 \times 4) = 7$ electrons to 4 atoms ; and

Ag_5Al_3 contains $(5 \times 1) + (3 \times 3) = 14$ electrons to 8 atoms ;
i.e. 7 electrons to 4 atoms.

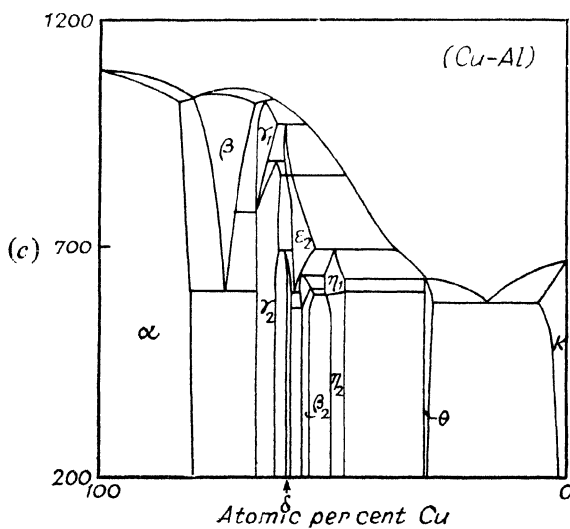
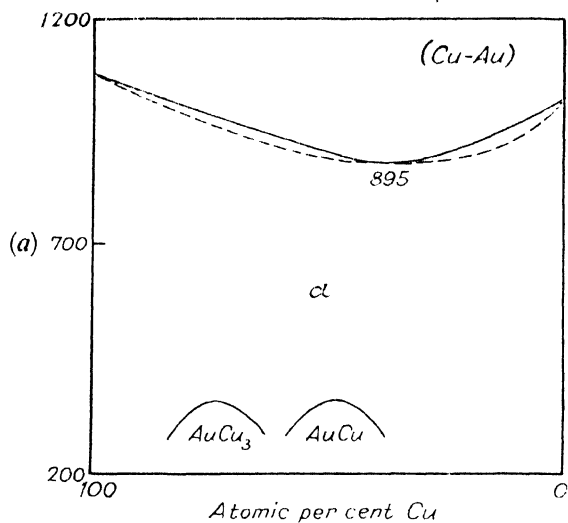
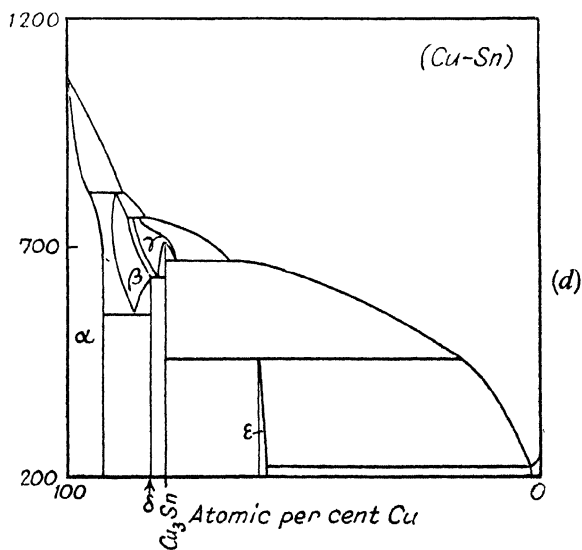
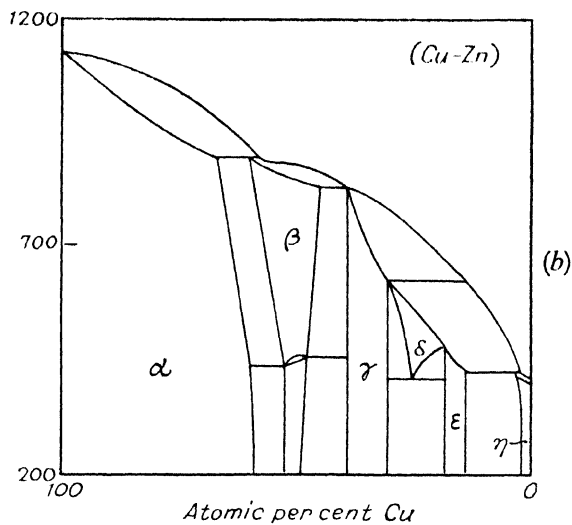


FIG. 34.—Equilibrium Diagrams for (a) Cu-Au, (b) Cu-Zn,



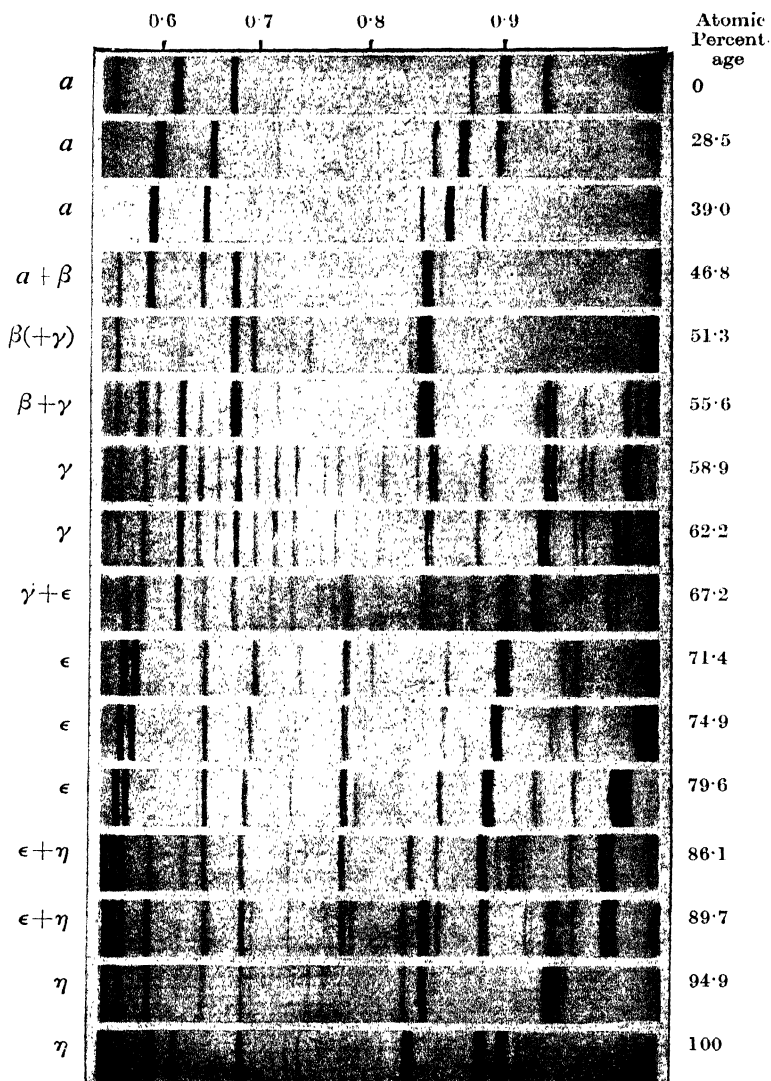
(Courtesy The Royal Society of Arts.)

(c) Cu-Al, (d) Cu-Sn Alloys. (Atomic per cent. Base.)

Electron Compounds containing Transition Series Metals.

There are a number of alloys of low valency metals like copper, silver and gold with higher valency metals like zinc, magnesium, cadmium, aluminium, tin, etc., in which are found phases based on electron compounds formed, in accordance with the Hume-Rothery Rules, with electron : atom ratios of 3 : 2, 21 : 13 and 7 : 4. The formation of the corresponding electron compound phases in the silver-cadmium alloys is shown in Fig. 35. It has also been found that the β -phase and γ -phase compounds of the transition metals, e.g. iron, cobalt and nickel, appear to obey the same Rules, *provided the atoms of these latter metals are regarded as contributing no valency electrons to the alloy electron cloud structure*. Examples of such compounds are FeAl (3 electrons—from the Al atom only—to 2 atoms) and Fe₅Zn₂₁ (42 electrons—from the Zn atoms only—to 26 atoms, so that the electron : atom ratio is 21 : 13). An explanation of this apparent anomaly lies in the fact that in the transition metals the *ions* have incomplete outer electron shells, so that the atoms may, for this reason, be very reluctant to give up electrons to the alloy electron cloud.

Structures of Abnormal Valency or Electron Intermetallic Compounds. We have seen how in many alloy systems the β -, γ - and ϵ -phases are based on electron compounds the formulae of which differ very widely but which have in common electron : atom ratios of 3 : 2, 21 : 13 and 7 : 4. The range of existence of the particular phases is really a range of solid solution in the compound concerned, and this tends to decrease, as it does in primary solid solution, with increase of valency of the second metal. The β -, γ - and ϵ -phases have, however, more in common than mere electron concentration, for they have, in addition, the same lattice structure, although the atomic arrangement is usually a purely random one. Thus, *the 3 : 2 β -compound phase is normally body-centred cubic*, although it may have a modified cubic structure known as the “ β -manganese” one ; the 21 : 13 γ -compound phase, known as the “ γ -brass” structure,



(Courtesy The Royal Society of Arts.)

FIG. 35.—Results of X-Ray Examination of Silver-Cadmium Alloys (Westgren), Showing Appearance of New Diffraction Pattern with Each New Electron Compound Phase. (Compare Cu-Zn Alloys, Fig. 34 (b)).

has a lattice unit containing 52 atoms per unit cell; and the 7:4 ϵ -phase compound has a close-packed hexagonal lattice. The lattice unit of the γ -brass structure may be regarded as being built up of 27 body-centred cubes—two atoms per cube—from which complex are removed two atoms, leaving 52 in all; the lattice unit may then be written as $4\text{Cu}_5\text{Zn}_8$. Typical electron compound structure data are summarised in Table XI.

TABLE XI.—STRUCTURE OF ABNORMAL VALENCY OR ELECTRON INTER-METALLIC COMPOUNDS

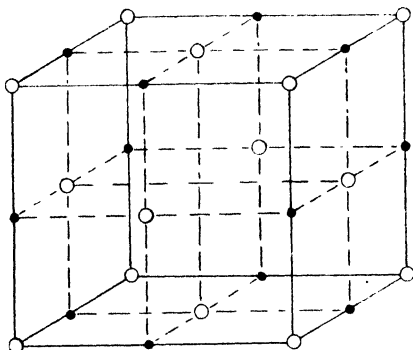
Phase Electron : atom Ratio Structure	β 3 : 2 b.c.c. β -Mn	γ 21 : 13 γ -brass	ϵ 7 : 4 c.p.h.
Cu-Zn	CuZn	Cu_5Zn_8	CuZn_3
Ag-Zn	AgZn	Ag_5Zn_8	AgZn_3
Au-Zn	AuZn	Au_5Zn_8	AuZn_3
*Ag-Cd	AgCd	Ag_5Cd_8	AgCd_3
Cu-Al	Cu_3Al	Cu_8Al_4	
Ag-Al			Ag_5Al_3
Cu-Sn	Cu_5Sn	$\text{Cu}_{31}\text{Sn}_8$	Cu_3Sn
Cu-Si	Cu_5Si	$\text{Cu}_{31}\text{Si}_8$	Cu_3Si
Co-Al	CoAl		
Co-Zn	CoZn_3	$\text{Co}_5\text{Zn}_{21}$	
Ni-Zn		$\text{Ni}_5\text{Zn}_{21}$	
Pt-Zn		$\text{Pt}_5\text{Zn}_{21}$	
Fe-Al	FeAl		
Ni-Al	NiAl		
Na-Pb		$\text{Na}_{31}\text{Pb}_8$	

* See Fig. 35, p. 99.

In conclusion, it may be stated that the succession of α -, β - and γ -phases does not apply to *all* binary systems, for size-factor *may*, in some cases, determine the composition of the compounds formed. This effect is well demonstrated in the compounds Cd_2Li , Cd_6Na and Cd_{11}K , where the number of cadmium atoms in the compound increases with the size of the alkali metal atom.

Interstitial Solid Solutions and Compounds. The next type of intermetallic compound to be discussed is the *interstitial compound*, which may be formed when the solute atoms are very much smaller than those of the solvent. The most common solute atoms of small diameter are those of *hydrogen*, *boron*, *carbon* and *nitrogen*, and many of their compounds with metals are characterised by very high melting-points and extreme hardness.

One way in which an interstitial solid solution may be formed in a face-centred cubic metal is illustrated in Fig. 36. The atoms of the solvent metal M are shown as ○ and those of the much smaller solute S as ●. The shortest interatomic distance, i.e. the atomic diameter, of the solvent M is given by $a\sqrt{2}/2$, where a is the lattice parameter of M (p. 58). The M atoms are separated by a distance a , along the cube edge, so that the length of side available for an atom of S is $a - a \cdot \sqrt{2}/2$



○ = Solvent metal ● = Solute

FIG. 36.—Interstitial Solid Solution in a Face-Centred Cubic Metal.

$= a(2 - \sqrt{2})/2 = 0.586a/2 = 0.293a$. The condition to be satisfied if the S atoms are to fill completely the available spaces between the M atoms is that the "diameter ratio"—i.e. the ratio of the diameter of the solute atom S to that of the solvent metal M—which may be written as d/D , must be equal to $0.293a$ divided by $a \cdot \sqrt{2}/2 = 0.293 \times 2/1.414 = 0.586/1.414 = 0.41$. If, therefore, the solute atom diameter is greater than $0.41 \times$ solvent atom diameter, the solvent lattice will tend to become distorted and to lose its cubic character. It has, in fact, been shown that if the diameter ratio exceeds 0.59, then the lattice

becomes complex in character. Again, if the diameter ratio is less than 0.41 the solute atoms will tend to be "loose" in space. Elements with very small atoms are therefore extremely unlikely to form interstitial solid solutions of the type shown in Fig. 36. In this particular lattice each S atom has six M neighbours at a distance equal to $0.5a$. Such a lattice, with all the available solute atom positions filled, is of the sodium chloride type (Fig. 28).

When the diameter ratio is less than 0.41 the \bullet atoms of solute S are more likely to take up some or all of the positions at the centres of the smaller cubes of Fig. 36. An S atom at the centre of one of these cubes would have *four* M neighbours at a distance $a \cdot \sqrt{3}/4 = 0.433a$, compared with $0.5a$ in the previously described interstitial lattice. In order to determine the necessary diameter ratio for the formation of this particular type of interstitial solid solution, we shall, for the moment, find it more convenient to think in terms of the radii of the M and S atoms. The atomic diameter of face-centred cubic M is $a \cdot \sqrt{2}/2$, so that the corresponding atomic radius is $a \cdot \sqrt{2}/4$, i.e. $0.354a$. If the S atoms are to fill all the available space they must have a radius equal to $0.433a - 0.354a$, i.e. $0.079a$. Under such circumstances the radius ratio, which is the same as the diameter ratio, must be equal to $0.079a/0.354a = 0.23$. If all of the smaller cube centres are occupied by S atoms, then the lattice would be of the fluor spar type (Fig. 29), while if only alternative smaller cube centres have S atoms, then the lattice would resemble that of zinc blend (Fig. 32).

It might be noted that it is possible for interstitial solid solutions of both of the previously described types to be formed in metals with close-packed hexagonal lattices, so that in the one case each S atom would have six M neighbours and in the other only four; the latter possibility can only be expected, as before, with the smallest of solute atoms. Body-centred cubic metals are less likely to form interstitial solid solutions. It seems that of the possible solutes hydrogen is the only one

with atoms small enough to have only four metal neighbours, and that boron, carbon and nitrogen, with atomic diameters of 1.98\AA , 1.54\AA and 1.40\AA respectively, form face-centred cubic, or close-packed hexagonal, interstitial lattices, so that each solute atom has six metal neighbours, if the diameter ratio is greater than 0.41 but less than 0.59; if the ratio is greater than 0.59, then more complex interstitial structures are formed.

We might here deal briefly with the structure of the well-known interstitial compound iron carbide, or cementite. The largest interatomic distance in iron is 2.52\AA , which figure may be taken for the atomic diameter of iron, while that of carbon is 1.54\AA , so that the diameter ratio is $1.54/2.52 = 0.61$; i.e. the diameter ratio is greater than 0.59. The relatively small size of the iron atom therefore induces the formation of an interstitial structure which is more complex than the simple cubic or hexagonal types described above.*

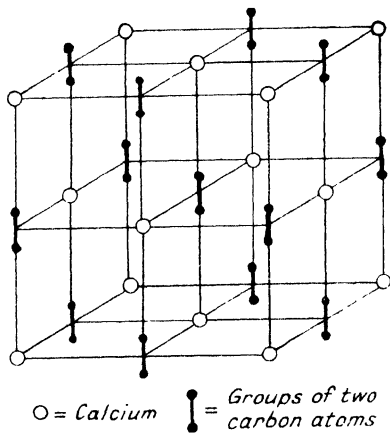


FIG. 37.—The Calcium Carbide Lattice.

Metal-like and Salt-like Interstitial Compounds. A different type of interstitial lattice structure—that of calcium carbide—is shown in Fig. 37, in which the face-centred cubic calcium atoms are shown as ○, and the interstitial carbon atoms are in groups of two. This type of lattice, in view of its slight vertical distortion, is face-centred tetragonal rather than face-centred cubic, but its most interesting feature is the fact that here the interstitial carbon atoms are linked together in groups of two.

* See Petch, N. J., "The Interpretation of the Crystal Structure of Cementite," *J.I.S.I.*, Adv. copy, February, 1944.

This leads to properties, both physical and chemical, which are entirely different from those of the metallic type structures previously described. These property differences must now be discussed in rather more detail.

It has been found that when the small-atom elements hydrogen, boron, carbon and nitrogen combine with transition series metals like titanium, tungsten, molybdenum, iron, etc., the compounds formed, e.g. TiC , W_2C , WC , Mo_2C , MoC , etc., are characterised by certain pronounced metallic properties. Compounds of the smaller elements with transition series metals may therefore be called *metal-like interstitial compounds*. When, however, the same small-atom elements combine with the more electropositive metals or metalloids the compounds formed are more like normal chemical salts. Such compounds, e.g. LiH , CaC_2 , AsH_3 and AlN , may therefore be placed in another group, viz. the “*salt-like*” *interstitial compounds*. *Metal-like interstitial compounds* may be made by heating the powdered metals to high temperatures in contact with boron, carbon or nitrogen (or ammonia), the powdered compounds being subsequently sintered, in an inert atmosphere, at even higher temperatures. These compounds have extremely high melting-points—e.g. tungsten carbide melts at over $3,000^\circ\text{C}$.—and are nearly as hard as diamond. Chemically they are extremely inert, but physically they strongly resemble metals, e.g. their electrical conductivity is high, but shows a decrease with rise of temperature. The compounds may even alloy with metals; thus, an alloy of tungsten carbide with cobalt is being increasingly used for the tipping of modern cutting tools.

The *salt-like interstitial compounds*, on the other hand, have entirely different properties: they are non-conductors of electricity and are easily decomposed by the action of water or dilute acids. Of this group, the salt-like carbides have been subject to much study and have been classified as follows: (i) Those which yield methane with water, e.g. Al_4C_3 ; (ii) Those which give acetylene with water, e.g. CaC_2 ; and (iii) Those

which give mixtures of hydrocarbons, and, in some cases, hydrogen as well, with water, e.g. Fe_3C . *These compounds possess ionic rather than metallic lattices*—the positive metal ions being packed between the negative carbon ions—and it is for this reason that they are characterised by the presence of the more strongly electropositive metals. Iron, and its neighbouring metals chromium, manganese, cobalt and nickel, form carbides which show some of the properties of the metal-like, and some of those of the salt-like, interstitial compounds. These carbides are, however, more closely related to the metal-like interstitial compounds, although they have neither the chemical stability nor the definite metallic character of the refractory carbides previously described. The relatively small size of the iron atom, as we have seen, gives cementite a complex lattice structure, differing from that of iron, and this may account for the modified metal-like characteristics of Fe_3C . Ni_3C is even less stable chemically and Co_3C cannot be isolated. The structure of Cr_3C_2 is interesting, in that it has been shown to have a chromium lattice through which run long zig-zag chains of carbon atoms. This is a structure which falls between that of the true metal-like compound and that of the salt-like carbides, the former being characterised by the presence of isolated carbon atoms and the latter by the presence of equally isolated groups of carbon atoms.

We might conclude this section by a very brief reference to other intermetallic compounds the formation of which is governed largely by the question of the sizes of the atoms concerned. These are generally formed when size-factors are neither too unfavourable nor too favourable. They may be classified as being of the A_3B , AB_2 or AB types, and in them it seems that the question of the actual geometrical packing of the atoms has the most powerful effect. Examples of such compounds are: NaPb_3 and CaSn_3 , Cu_2Mg and KBi_2 , and NaTl and LiZn .

CHAPTER IX

THE PHYSICAL THEORY OF METALS

Objects of Physical Theory. We are now able to end our introductory survey of the fundamental structure of metals and alloys by referring briefly to the modern physical theories, for it is in these that we find *explanations* of the phase changes in alloy systems which take place in accordance with Hume-Rothery's empirical rules.

Atoms and Spectra. We started our discussion by a study of the structure of the atom based on chemical properties and on the indications of the periodic table (Chapter I), and we referred to Rutherford's original theory of the nuclear atom and to the modifications which were applied by Bohr and Sommerfeld in order to keep the chemical theories in line with contemporary physics. Since the study of the physics of atomic structure probably owes more to spectrum analysis than to any other method of approach we must now deal briefly with the physical interpretation of spectra.

When the light emitted by an incandescent solid is examined through a prism, a continuous spectrum is found, the colours gradually merging from red to orange, orange to yellow, and so on, and ending with blue to indigo and indigo to violet. This continuous light spectrum has been compared to the continuous "sound spectrum" produced by a full symphony orchestra when all the instruments are being played together. Thus, from the electronic viewpoint, the fundamental structure of an incandescent solid is extremely complex. However, it is possible to obtain much simpler light spectra in just the same way as a far less complex "sound spectrum" is produced by the symphony orchestra, when, for example, only the violins are being played. The instruments which produce the least

complex light spectra are the relatively free atoms of incandescent gases, and the simplest spectrum of all is given by incandescent hydrogen. The hydrogen spectrum consists of a series of apparently single bright lines, separated by dark spaces, as shown in Fig. 38. It is possible to measure the wavelength λ and calculate the frequency ν of the light which produces each of the H_α , H_β , H_γ , etc., bright lines, and to express the frequencies (for the so-called Balmer Series of Hydrogen Lines) in the form of the equation: $\nu = R(1/2^2 - 1/n^2)$, where n may be 2, 3, 4, etc., and R is the well-known Rydberg constant ($R = 3.29 \times 10^{15}$ vibrations per second).

Rutherford had suggested that the extra-nuclear electron in the hydrogen atom can rotate in orbits around the nucleus, and Bohr was able to follow this up by showing that the Balmer



FIG. 38.—The Hydrogen Spectrum.

(and other) Series could be explained by assuming that each orbit could only be occupied by an electron with a particular quantum of energy. Thus, in incandescent hydrogen, electrons may be "excited" and driven outwards to other orbits. Their sudden return would be accompanied by a release of energy in the form of light, the frequency of which would depend on the respective energies, as indicated by their quantum numbers, of the orbits concerned. For example, the wavelength of the light emitted by the return of an "excited" electron from the third orbit to the second (Fig. 39 (a)) can be calculated from its frequency as given by the Balmer Series equation: $\nu = R(1/2^2 - 1/3^2) = 3.29 \times 10^{15}(1/4 - 1/9) = 45,700 \times 10^{10}$ vibrations per second. This is the H_α line, and the H_β , H_γ and H_δ lines are produced by the return to the second orbit (quantum number 2) of electrons from orbits with quantum numbers 4, 5 and 6 re-

spectively. There were subsequently discovered in the hydrogen spectrum two more series of lines: the Lyman Series in the ultra-violet region to the right of the portion of the spectrum shown in Fig. 38, and the Paschen Series in the infra-red region to the left of it. Their formation was similarly explained, the

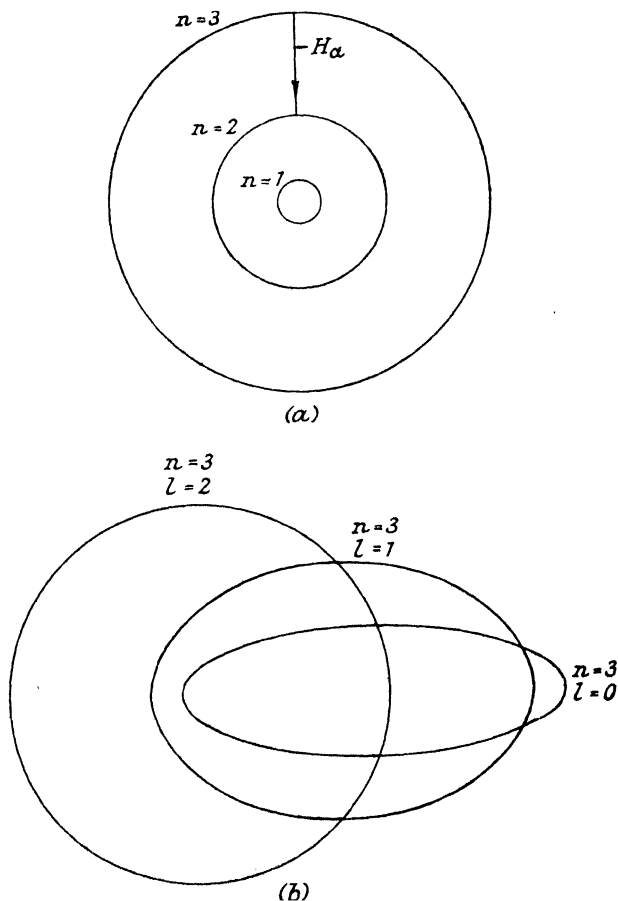


FIG. 39.—(a) Formation of $H\alpha$ Line by Electron Jump from M to L Shell.
(b) Sub-Level Orbits in the Third Main Shell.

Lyman Series lines being formed by the return of electrons to the orbit of quantum number 1, with frequencies given by $\nu = R(1/1^2 - 1/n^2)$, and the Paschen Series being produced by the jumping of electrons from outer orbits to the orbit with quantum number 3.

Principal and Subsidiary Quantum Numbers. Careful examination of even these simple spectra showed that what were first considered to be single lines could, in fact, be shown to consist of groups of even finer lines. This immediately suggested that while the general orbital energy levels remain as originally postulated, there are possible sub-levels within each group, the differences between the energies of these being small compared with the energy differences between any two main levels. The "fine structure" of any one line in the hydrogen spectrum would then be caused by the jumping of electrons from, for example, one definite outer energy level into the different sub-levels of an inner one. It was in order to picture the existence of these sub-levels that Sommerfeld introduced the possibility of electron orbits being elliptical as well as circular. He suggested, in fact, that an orbit would be characterised by a principal quantum number n and a subsidiary quantum number k , k being able to have any numerical value from 1 to n . It was shown that the major axis of the ellipse is proportional to n and the minor axis to k . Thus, when n and k are numerically the same the orbit is circular, and, for a given n , as k falls to 1 the ellipse becomes more and more eccentric. The subsidiary quantum number k was subsequently replaced by the azimuthal quantum number l , equal to $k - 1$; the maximum value for l , for a given n , is $n - 1$, and under the same condition its minimum value is 0. Hence, each energy level of principal quantum number n has, as before, n sub-levels. Again, the sub-level orbit will be a circle when $l = n - 1$, and an eccentric ellipse when $l = 0$. The sub-level orbits for the third main energy level ($n = 3$) are illustrated in Fig. 39 (b). It might be noted that the energies of electrons moving in each of the three illustrated

orbits are of the same general order of magnitude, but that there is a definite and quantised, though small, increase of energy as we consider first the circular 3_2 orbit, then the 3_1 orbit, and finally the markedly eccentric elliptical 3_0 orbit.

The electron shells of general energy level characterised by the principal quantum numbers $n=1, 2, 3, 4, \dots$ etc., are known as the K, L, M, N, \dots etc., shells respectively. In the K shell, which is nearest to the nucleus, $n=1$, so that l , which can have any value up to $n-1$, can only be zero. The L shell, with $n=2$, contains the two orbits: $n=2, l=1$ and $n=2, l=0$, viz. the 2_1 orbit (circular) and the 2_0 orbit (ellipse). Similarly, the M shell has the three sub-level orbits: $3_2, 3_1$ and 3_0 , and the N shell the four sub-level orbits: $4_3, 4_2, 4_1$ and 4_0 .

Magnetic and Spin Quantum Numbers. The discovery of the fine structure of the lines of the hydrogen spectrum led to the idea of the existence, for each main energy level after the first, of elliptical as well as circular orbits. It was later found that when a substance which is emitting radiation is placed in a strong magnetic field (Zeeman Effect) or in an electric field (Starke Effect) the lines may be split still further. This was then explained by assuming that the different n_l orbits, which may behave like small magnets, can, when subjected to the influence of magnetic or electric fields, *suddenly swing* rather than *gradually move* into definite angular positions. The number of such positions, for a given main energy level, and each characterised by a magnetic quantum number m , is given by $2l+1$. Thus, the 3_2 orbit (Fig. 39 (b)) may occupy any one of $2 \times 2 + 1 = 5$ planes, equally spaced around the nucleus. Its electron may rotate in the plane of the paper, as shown in Fig. 39 (b), or in one of the four other evenly spaced planes which intersect that of the paper. The 3_1 orbit may occupy any one of $2 \times 1 + 1 = 3$ planes, and the 3_0 orbit can only be found in $2 \times 0 + 1 = 1$ plane. The planes available for the three orbits of the M shell are therefore in number equal to $5 + 3 + 1 = 9$.

The position in space of the orbit, or rather the energy of

the electron due to the spatial arrangement of the orbit, is indicated by the magnetic quantum number m , which may, in fact, have any value from $-l$ to $+l$, e.g. $-l$, $-(l-1)$, $-(l-2)$,, 0 , $(l-2)$, $(l-1)$, l . There are, thus, for any given value of l , $2l+1$ spatial positions for the sub-level orbit.

Having now seen how was developed the quantisation of the main energy levels (viz. the K, L, M, N, etc., levels), of the sub-levels (with l equal to $0, 1, 2, 3$, and known respectively as the s, p, d, f sub-levels), and of the position in space of the electron orbit as indicated by the m quantum number, we must now deal briefly with the fourth and last quantum number—the spin quantum number s . It has been suggested that an electron, while rotating in its orbit around the nucleus, is capable of *spinning* on its own axis. Since there are only two alternative directions of spin, clockwise or anticlockwise, and since quantum numbers may differ only by whole numbers, s may only have one of the two possible values $+\frac{1}{2}$ or $-\frac{1}{2}$, depending on the actual direction of spin.

The Physical Interpretation of the Periodic Table. We can now see, by referring to Table XII, how these ideas, which started by explaining the possible positions of the extra-nuclear electron in the hydrogen atom and have since been extended to deal with the corresponding electrons of other atoms, have shown the numbers of individual extra-nuclear electrons which may be accommodated in the main energy levels of different atoms.

TABLE XII.—NUMBERS OF ELECTRONS IN COMPLETED K, L, M, N SHELLS

Electron Shell	K	L	M	N
Principal quantum no. n	1	2	3	4
Azimuthal quantum no. l	0	0 1	0 1 2	0 1 2 3
No. positions per orbit m	1	1 3	1 3 5	1 3 5 7
No. opposite spin electrons $s \pm \frac{1}{2}$	2	2 6	2 6 10	2 6 10 14
Total no. electrons per shell	2	8	18	32

It was postulated by Pauli that no two electrons in a single atom can have the same values of all four quantum numbers. Here we have, therefore, a physical interpretation of the periodic table and an explanation of the accommodation of a maximum of *two* electrons in the *first* shell, *eight* electrons in the *second* shell, *eighteen* electrons in the *third* shell and *thirty-two* electrons in the *fourth* shell (pp. 17 and 19). It has already been mentioned that it is convenient to refer to the sub-group electrons, pictured as being in orbits of decreasing eccentricity, as *s*, *p*, *d* and *f* electrons, the letters themselves being derived from the words “sharp,” “principal,” “diffuse” and “fundamental” used to describe spectra. In any main energy level the $l=0$ electrons are called the *s* electrons, the $l=1$ electrons the *p* electrons, the $l=2$ electrons the *d* electrons, and the $l=3$ electrons the *f* electrons. Thus, the *complete third main energy level*—the *M level*—accommodates two *s* electrons, six *p* electrons and ten *d* electrons. This level is, for example, incomplete in the case of the iron atom, when it only contains two *s* electrons, six *p* electrons and six *d* electrons. The extra-nuclear structure of the iron atom consists of two *s* electrons in the *first* main level, two *s* and six *p* electrons in the *second* main level, two *s* with six *p* and six *d* electrons in the *third* main level, and two *s* electrons in the *fourth* main level. This information may to some extent be summarised by stating that the extra-nuclear structure of the iron atom is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$. It may be of interest to compare this with the extra-nuclear structure of the iron atom as derived from purely chemical reasoning, given on p. 17.

Quantum Mechanics. While the previously described theory gives a most convenient picture of the possible arrangements of the extra-nuclear electrons of the different atoms, it must be mentioned that it has, within recent years, been to some extent replaced by the theories of wave mechanics. In just the same way as light sometimes behaves as particles and at other times as waves, so electrons can, for example, behave as

particles in the cathode ray tube (p. 10) and as waves in the electron microscope. The wave mechanics theory of atomic structure is highly mathematical, but fortunately its deductions are in very close agreement with those of the Bohr-Sommerfeld theory outlined above. It is for this reason only necessary to remind the reader that the ideas of particular electrons moving in definite geometrical orbits do not, of necessity, represent the *actual* state of affairs within the atom, but they do give a theory which is in conformity with most of the so-far established facts. So much, then, for the theory of atomic structure; we must now bring our discussion to its conclusion by dealing briefly with the modern physical interpretations of some of the properties of such aggregates of atoms as are found in solid metals and alloys.

Electrical Conductivity. Metal crystals have already been shown to consist of (a) positive ions arranged on a characteristic ordered lattice, and (b) an equivalent number of free electrons, which we have described as forming the metallic electron cloud. These free electrons behave in many ways like the molecules of a gas, and it is interesting to note that it has been found possible to apply to them the kinetic theory of gases. This has resulted in the building up of an "electron gas theory," but this cannot, however, be further discussed here.

The relatively good electrical conductivities of metals are due almost entirely to the presence of the free electrons in the electron cloud. They can be caused to move, i.e. an electric current can be made to flow, by the application of much less energy—i.e. a lower electromotive force—than would be needed to bring about actual *separation* of the electrons from their outer orbits. Electrical insulators have crystal lattices in which there are no free electrons. Thus, for example, in fused silica all the valency electrons are "tied up" in holding the silicon and oxygen atoms together. Here we have an explanation of the fact that the electrical conductivity of the metal copper is about 10^{24} times greater than that of the insulator fused silica.

There are, in fact, good reasons for believing that the electrical conductivity of a substance depends mainly on the number of free electrons present per unit volume, i.e. on the electron concentration, when the latter is expressed on a volume basis rather than as the number of electrons per atom, in which connection the term has previously been used in this book.

Thermal Conductivity. Just as metals are good conductors of electricity so they are good conductors of heat. The conduction of heat was once thought to be due to the transmission of energy of vibration from one atom to its neighbours. If this were indeed the mechanism of thermal conductivity there seemed to be no good reason why atoms of metals should transmit energy of vibration any more readily than atoms of non-metals of similar weight. We find, however, that in general non-conductors of electricity are poor conductors of heat. This immediately suggests that in thermal conductivity heat energy is transmitted very largely by means of free electrons and only to a much smaller extent by its passage from one atom to the next. It can, in fact, be deduced from theoretical considerations that, at a given temperature, the *ratio* of the electrical to the thermal conductivity of a pure metal is constant, and is independent of the nature of the metal concerned. This was actually demonstrated experimentally and was expressed in the form of the well-known law of Wiedermann and Franz. In the case of alloys it has been shown that the electrical-conductivity/thermal-conductivity ratio deviates slightly from that required by the Wiedermann-Franz Law. It has, however, been found possible to relate directly electrical and thermal conductivities of alloys by an equation of the type: $K_T = 5.02 K_E T \times 10^{-9} + 0.03$, where K_T =thermal conductivity, K_E =electrical conductivity and T is the absolute temperature. Thus, while electrical conductivity is *entirely* a function of the electron cloud in the metal or alloy lattice, thermal conductivity is *largely* a function of the same electron cloud. Alloying affects both these physical properties in the

same direction and to almost the same extent. The slight difference in the functions of the electron cloud in the two cases accounts for the slight deviations from the Wiedermann-Franz Law.

Specific Heat. As long ago as 1819 Dulong and Petit established that there is a definite relationship between specific heat and atomic weight. They established the law that, for nearly all the elements, the product of specific heat and atomic weight is approximately equal to 6. One notable exception to the rule was found to occur in the case of the element carbon, but even here the product—the atomic heat—tended at high temperatures to approach the stated value. Since specific heat usually increases with rise of temperature, the product of specific heat and atomic weight is of necessity only approximate. The point to be emphasised, however, is that, within its limits, the law is true for all solid aggregates of atoms, whether those atoms be metallic or non-metallic in nature. We thus find that only metals and alloys, with their characteristic lattices, show good electrical and thermal conductivity, while non-metals are poor conductors in each case. On the other hand, from the specific heat point of view, there is nothing to choose between metals and non-metals. It would therefore appear that the absorption of heat energy, with its consequent rise of temperature, does not require in any way the presence of an electron-cloud type lattice. It seems, in fact, that the free electrons of a metallic lattice participate in the energy changes involved in thermal and electrical conductivity, while they do not take part in the energy changes associated purely with rise or fall of temperature. In other words, temperature changes are associated with changes of atomic or ionic vibration and do not normally affect the “free” electrons.

The Modern Theory of Alloys. We thus find that electrical conduction indicates that, in a metallic lattice, the cloud electrons are *free*, while specific heat suggests, since they do not normally take part in the absorption of heat energy, that they are *fixed*.

This apparent contradiction leads to the conclusion that a metal lattice is, in the normal ranges of temperature, *filled* with electrons in much the same way as, in the case of the heavier atoms, the inner energy levels are *filled* with their electrons ; this is why the cloud electrons are not normally affected by the relatively small energy increments associated with heating. In other words, in the metal lattice there are definite electron energy levels, which are just as fundamental, and from some points of view just as important, as the energy levels in atoms. This important idea will now be discussed in rather more detail.

The electrical and optical properties of metals and alloys require that they should contain free electrons comparable in number with the atoms present. It is these electrons which are responsible for electrical conductivity, but which are not normally affected by rise of temperature. We may reasonably suppose that the cloud electrons are in a continual state of motion and that they therefore possess kinetic energy. We shall, indeed, soon find that, in accordance with the above suggestion, the permitted energies of these electrons are quantised in much the same way as those of the extra-nuclear electrons in a free atom. It is possible, in *theory* only, to consider the building up of an atom by starting with a nucleus and then supplying the requisite number of orbital electrons. Similarly, and also in *theory* only, we can build up a metal by starting with a metal ion lattice and admitting to it the necessary number of valency electrons. It is understandable that the first electrons will be readily accepted—they need not be projected into the ion lattice with high kinetic energies—but the addition of more and more electrons should gradually become increasingly difficult. We might well ask whether there is any limit to the number of cloud electrons which can be taken up by a given ion lattice, and, if so, are we able to calculate where that limit should be?

An affirmative answer can be given to both these questions. The problem is conveniently approached along the lines sug-

gested by N. F. Mott. The valency electrons move through a metal lattice with various velocities *up to a certain maximum*. It has been previously mentioned that electrons can, like light and X-rays, be diffracted, so that to each velocity there corresponds a certain wavelength. Thus, the electron cloud wavelengths have a series of values *down to a certain minimum*. This follows from the fact that, in general, the shorter the wavelength the higher the frequency, and the higher the frequency the greater the transmitted energy. X-rays, for example, transmit more energy than does light, and light transmits more energy than do radio waves. The more we try to increase the number of cloud electrons in our hypothetical ion lattice, the greater is the energy with which we must project them. In other words, the more electrons there are in any volume, *the smaller will the minimum wavelength be*. It has been shown that this minimum wavelength can be calculated from the formula :

$$\lambda_{min} = 2 \times \sqrt[3]{\pi V / 3 N_E} \quad . \quad . \quad . \quad . \quad (1)$$

where N_E is the number of electrons in a volume V .

We have, so far, been largely concerned with the hypothetical case. We now are able to deal with the exceedingly practical one of alloying, such as occurs, for example, in the addition of zinc to copper. Every added zinc atom brings into the lattice one extra valency electron. If, therefore, we continue to increase the concentration of zinc we increase the number of electrons N_E , and hence must *decrease* the minimum wavelength λ_{min} . We must eventually reach a point when the fastest electrons have a wavelength of the same order as the distance apart of the atoms, so that, like the corresponding X-rays, they undergo Bragg reflection when normally incident to certain planes of the lattice. This state of affairs is one which the crystal will, if possible, avoid by changing its structure.

This electron cloud "saturation point" argument may now be applied to the characteristic metallic lattices, and we shall deal first with the face-centred cubic or cubic close-packed

lattice. In this lattice reflection takes place first from the (111) planes (*vide* pp. 48 and 53), these being the most widely spaced and distant $a/\sqrt{3}$ apart, a being the lattice constant.

The condition for Bragg reflection (p. 32) is $n\lambda = 2d \cdot \sin \theta$. If we now consider electron-waves incident normally to the (111) planes we have $\theta = 90^\circ$, and therefore $\sin \theta = 1$, while $d = a/\sqrt{3}$, so that for first order reflection (diffraction) with $n = 1$, $\lambda_c = 2a/\sqrt{3}$, where λ_c is the *critical* wavelength corresponding to the highest energy electrons allowed in this lattice. Since in face-centred cubic metals there are four atoms per lattice unit we may express a in terms of V as follows: $a = \sqrt[3]{V/N_A/4} = \sqrt[3]{4V/N_A}$, N_A being the number of atoms per volume V . Comparing this result with that of equation (1) we see that reflection will take place when the number of electrons is such that: $2 \times \sqrt[3]{\frac{\pi V}{3N_E}} = \frac{2}{\sqrt{3}} \times \sqrt[3]{\frac{4V}{N_A}}$, which is easily simplified to :

$$N_E/N_A = \pi\sqrt{3}/4 = 1.362 \quad . \quad . \quad . \quad (2)$$

This is very near the actual value of 1.4 for the electron concentration at which certain α -solid solutions become saturated. In view of this remarkable correlation of theoretical calculation and experimental data the author feels that he might be excused the repetition of a sentence from p. 70 : " It may therefore be concluded that, for solid solutions in copper and silver, the maximum solid solubility of the metals in Groups IIB, IIIB and IVB (*of the Periodic Table*) with favourable size-factors is found when the electron concentration is 1.4." Experimental data for a number of alloys are given in Table XIII below, and show remarkable agreement with the above theoretical calculation.

There is therefore a *theoretical* basis for the saturation of alpha solid solutions at an electron concentration, i.e. an electron : atom ratio, of 1.4. A similar treatment has been successfully extended to the other phases, and thus there has, within recent years, been provided an explanation for the

empirical Hume-Rothery Rules (p. 94). These, it will be remembered, indicated that the fundamental intermetallic compounds on which are based the β , γ , etc., phases are encountered at electron : atom ratios of 3/2, 21/13 and 7/4. We can now proceed to examine the theoretical basis for these ratios. Thus, for example, in the body-centred cubic β -phase, electron-wave reflection takes place first at the (110) planes, distant $a/\sqrt{2}$ apart (p. 49). Bragg reflection takes place when $n\lambda = 2d \cdot \sin \theta$, and this time it is readily shown that the condition for reflection is that λ_c , the minimum wavelength, is equal to $2a/\sqrt{2}$. In the body-centred cubic lattice there are two atoms per lattice unit, and we may write $a = \sqrt[3]{\frac{2V}{N_A}}$, so that

$\lambda_c = \frac{2}{\sqrt{2}} \times \sqrt[3]{\frac{2V}{N_A}}$, N_A being, as before, the number of atoms per volume V . But, from equation (1), $\lambda_c = 2 \times \sqrt[3]{\frac{\pi V}{3N_E}}$, and normal reflection will take place when : $\frac{2}{\sqrt{2}} \times \sqrt[3]{\frac{2V}{N_A}} = 2 \times \sqrt[3]{\frac{\pi V}{3N_E}}$, and

$$\text{hence} \quad N_E/N_A = \frac{\sqrt{2} \cdot \pi}{3} = 1.480 \quad . \quad . \quad . \quad (3)$$

The body-centred cubic lattice is thus stable over a wider range than the face-centred cubic one, and should not, in fact, become unstable till the electron concentration, as indicated by the Hume-Rothery Rule, is of the order of $\frac{3}{2}$. Supporting data in summarised form are also included in Table XIII.

It has been calculated, by these and other methods, that the critical electron concentrations for phase change in alloy systems are as follows :

For face-centred cubic α -phases	1.362
For body-centred cubic β -brass and β -Mn structures	1.480
For the complex γ -brass structures	1.538
For the ϵ -phases	1.75

It may, incidentally, be mentioned that, in order to explain the various intermetallic compound formulæ, the Hume-Rothery ratios have been simplified to whole-number ratios; their derived phases, however, do, in fact, have a range of composition on either side of that of the particular individual compound concerned.

TABLE XIII.—ELECTRON CONCENTRATIONS OF CORRESPONDING PHASES IN VARIOUS ALLOY SYSTEMS

Alloy System	Maximum Electron Concentration α -Phase	Lower Limit of β -Phase	Boundaries of γ -Phase
Cu-Zn	1.38	1.48	1.58-1.66
Cu-Al	1.41	1.48	1.63-1.77
Cu-Sn	1.28	1.49	1.67-1.67
Cu-Si	1.42	1.49	—
Ag-Zn	1.43	1.50	1.59-1.63
Ag-Cd	1.38	1.50	1.58-1.63
Ag-Al	1.41	—	—
Ag-Sn	1.37	—	—
Calculated Electron Concentration	1.362	1.480	1.538
Hume-Rothery Ratio	1.40	1.50	1.615

It will be noted from the above table that in many cases the phase change does not occur immediately the calculated electron concentration is reached. It would seem quite reasonable to assume that a certain small excess of added electrons, over and above the calculated number, is often required in order to overcome the individual phase's inherent inertia towards structural change.

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